

CANADIAN JOURNAL OF RESEARCH

VOLUME 19

MARCH, 1941

NUMBER 3

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NATIONAL RESEARCH COUNCIL
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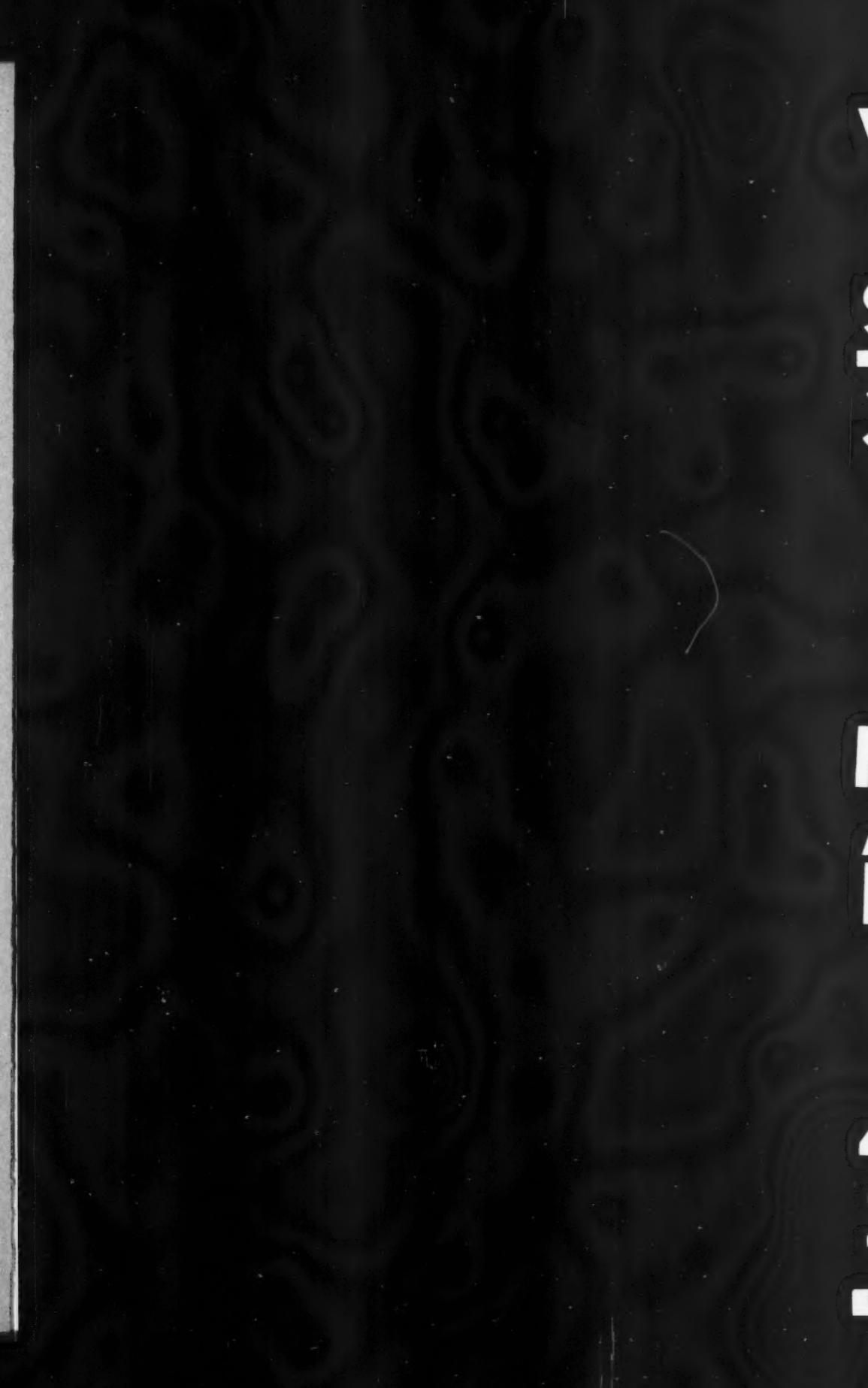
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Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 19, SEC. A.

MARCH, 1941

NUMBER 3

THE CAPTURE CROSS-SECTION FOR THERMAL NEUTRONS OF CADMIUM, LITHIUM⁶, BORON¹⁰, BARIUM, MERCURY AND HYDROGEN¹

BY E. L. HARRINGTON² AND J. L. STEWART³

Abstract

A comparison method of measuring, by using solutions, the capture cross-sections for thermal neutrons is described. The chief advantages are directness, simplicity, and freedom from uncertainties as to direction of path, or as to the magnitude of the scattering effect. The method is best suited to nuclei of large cross-sections. Assuming the well checked value for the cadmium nucleus to be correct, the capture cross-sections of certain other nuclei were determined. The results for barium and for hydrogen differ widely from values previously published.

Most determinations of the cross-sections for capture of thermal neutrons by various nuclei have been made by the use of materials in sheet form. Amaldi and Fermi (1, 2) employed absorbers placed near the sources of neutrons. Dunning and his co-workers (4) used arrangements that provided for greater distances between the source and the detectors, and hence reduced considerably the uncertainties as to the direction of the incident neutrons. In all such determinations two difficulties are inherent. It cannot be determined accurately how much of an observed absorption is due to the scattering of the neutrons and how much to their capture, nor is there any certainty as to the paths travelled by the neutrons through the absorber, since generally a large number of scattering impacts are suffered by a neutron before the final impact that results in its capture. The extent to which such factors affect the results also varies from element to element, since the thickness chosen for any absorber must depend on the total cross-section of its nuclei if the magnitudes of the absorption effects are to be kept within suitable ranges. Because of the uncertainties involved, the errors may range up to 10 or even 25% in the case of strong absorbers (4, p. 277).

The solution method of comparing capture cross-sections of nuclei offers many advantages and has been proposed or used along two or more lines. Furry (6) in 1936 suggested the principle involved. In 1938, Frisch, Halban, and Koch (5) and also Knauer (7) published results obtained by using solutions of the absorbing element. It is believed that the method, employed in the investigation herein reported, and which is due in part to Professor Goudsmit, involves certain additional modifications of importance.

¹ Manuscript received November 20, 1940.

Contribution from the Department of Physics, University of Saskatchewan, Saskatoon, Sask.

² Professor of Physics, University of Saskatchewan.

³ Research Student and Technician for Radon Plant, Saskatchewan Cancer Commission, Saskatoon, Sask.

Theory of Experiment

When fast neutrons move through a hydrogenous material like paraffin or water their speeds are rapidly reduced to those corresponding to thermal conditions (1, 2). However a thermal neutron may make many additional elastic impacts without further change in energy before making the inelastic impact that results in a deuteron. This means that in a hydrogenous medium subject to the bombardment of fast neutrons there accumulates a certain concentration of thermal neutrons, which may be represented by c , where c is the number per cubic centimetre.

The value of $\frac{dc}{dt}$ will depend mainly on three factors: (i) the gain in neutrons due to the diffusion of thermal neutrons from adjacent space, (ii) the gain due to the slowing down of fast neutrons entering the space, and (iii) the loss due to captures by hydrogen or other nuclei. A general differential equation covering these factors may be written as follows:

$$\frac{dc}{dt} = D \left[\frac{d^2c}{dx^2} + \frac{d^2c}{dy^2} + \frac{d^2c}{dz^2} \right] + KS - Bc,$$

where D is the diffusion constant for thermal neutrons, KS the rate at which the unit volume acquires thermal neutrons through the slowing down of fast neutrons from a source of strength S , and B is a constant such that Bc gives the rate of capture.

For a steady state $dc/dt = 0$. Also, if the experimental arrangements are such as to eliminate or at least greatly reduce any effect of diffusion, as is the case for the twin sources employed in the work herein described, then the

equation simplifies to $KS = Bc$ or $\frac{1}{c} = \frac{B}{KS}$.

The probability of capture, B , must depend on the total capture cross-section present in the unit volume, and may be written $\sum N_i \sigma_i$, where N_i is the number of nuclei of substance i per cubic centimetre, each having a capture cross-section of σ_i . In a pure water medium N_H would be taken as the number of hydrogen nuclei, the oxygen nuclei being neglected because of the very small value of σ_O . In a water solution, say of cadmium, B becomes $N_H \sigma_H + N_{Cd} \sigma_{Cd}$. For additional substances in solution additional terms must be added. Experimentally the relative values of c were determined by introducing into the solution a detector, whose induced radioactivity, a , due to exposure for a fixed time, may be taken as proportional to c . If a be the numerical value of the activity measured in any convenient empirical units, and if S is constant, then for a given series of observations obtained by changing the concentration of a solution of cadmium,

$$\frac{1}{a} = K'(N_H \sigma_H + N_{Cd} \sigma_{Cd}),$$

where K' is a new constant of proportionality. Since $N_H \sigma_H$ and σ_{Cd} are constant it follows that $1/a$ plotted against N_{Cd} should give a straight line

such as PM in Fig. 1. When $1/a$ is zero, $\sigma_H = \frac{-N_{Cd(H)}}{N_H} \sigma_{Cd}$, where $N_{Cd(H)}$ is the value of N_{Cd} that would effect the same capture as the hydrogen of the water. $N_{Cd(H)}$ may be read from OP . N_H is known from Avogadro's number. Hence, assuming the published value (7) of σ_{Cd} to be correct, the value of σ_H may be directly computed provided that all losses in neutrons in pure water are due to captures by hydrogen nuclei. Actually the plateau of uniform concentration is finite and there must be some diffusion losses. Any such will tend to give σ_H an apparent value higher than its true value.

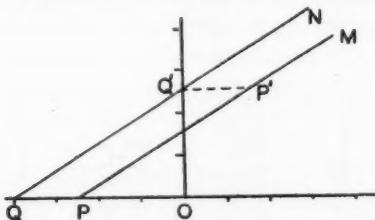


FIG. 1. Graphical method of comparing capture cross-sections.

The method may be applied also to the determination of the value of the capture cross-section of the atomic nucleus of an element J by employing initially a solution of J of known concentration in place of the pure water. This should give a new line parallel to PM , as QN . The increase in the intercept PQ (or $P'Q'$) gives directly the value $N_{Cd(J)}$ of N_{Cd} that would offer the same total capture cross-section as N_J of the J atoms that were placed in a unit volume of the solution. From this it follows that $\sigma_J = \frac{-N_{Cd(J)}}{N_J} \sigma_{Cd}$. In a similar way a σ_K might be obtained, and as a cross check, $\sigma_J + \sigma_K$. The uncertainty mentioned in the paragraph next above will not enter here since only the difference in intercept is involved.

Apparatus

The two principal items of the equipment were an Edelmann electrometer, with its connected ionization chamber, and an exposure tank with its accessories and the sources. The former was practically equivalent to that described by Amaldi and Fermi (1, 2). The more essential features of the latter are represented by Fig. 2.

The two beryllium-radon sources S_1 and S_2 are mounted at such a distance apart that the concentration of neutrons throughout the region of the silver detector D is substantially constant, as required by the theory of the experiment. The glass jar surrounding these contained the test solutions and could be drained readily by lifting the ground glass plug P . This and the fixed guides for the detector support rod were mounted within a water tank on suitable supports as shown. No metal other than the detector was included with the inner jar, as any change in the concentration of the solution through

ion replacement must be prevented. The detector had a diameter of 50 and a thickness of 0.15 mm.; a thin coat of Duco was applied to it. S_1 and S_2 contained substantially equal quantities of beryllium granules and also like quantities of radon (about 150 m.c. each at the beginning of a series). An electric timing system subject to dual control was available. Ample protective shielding was provided for the observers and the electrometer system.

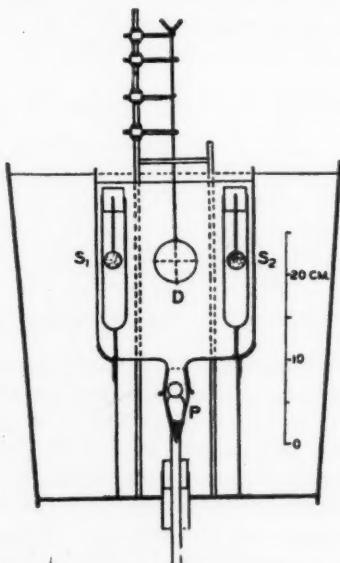


FIG. 2. Diagrammatic representation of the arrangement of the equipment, sources, and solutions used in exposing detectors to the neutronic radiation.

Experimental Procedure

Briefly stated, the essential steps in any measurement of the relative concentration of thermal neutrons included merely the exposure of D and the subsequent measurement of its relative activity. The steps were carried out in a manner very much like that reported by Amaldi and Fermi, and need not be described in detail. These involved the exposure of D in the position shown in Fig. 2 for exactly 120 sec., followed 16 sec. later (the time found necessary in practice to remove, dry, and then transport the detector to the somewhat distant electrometer system) by an observation of the rate of deflection of the electrometer fibre due to the induced radioactivity of D . For each determination a number of check runs (usually six) were made. This was followed by a set of measurements similar except that D was shielded on each side by a disk of cadmium sufficiently thick to absorb the thermal neutrons. From this set it could be ascertained how much of the activity first observed was due to fast neutrons. The difference in the two rates of deflection gave a measure of the radioactivity, a , acquired by D due to the

slow neutrons alone, and therefore of their concentration (see Refs. 1, 2). The sensitivity of the electrometer was constantly checked by means of a Ra D standard and due allowance made for the decay of the radon.

Since these comparisons of capture cross-sections of nuclei hinge on an accurate knowledge of their numbers per unit volume, great care was required in the preparation of the solutions employed. Trial runs showed that cadmium solutions ranging up to say 20×10^{18} nuclei per cubic centimetre gave absorptions of suitable magnitude. The concentrations of the subsequently added ions of lithium, boron, etc., were so adjusted as to give effects of the same order of magnitude as that due to the cadmium solutions, hence were varied roughly inversely as their corresponding capture cross-sections.

Attention should be called to certain practical difficulties with respect to the preparation of solutions. Each metal should be introduced into the solution in the form of one of its soluble salts and the salt most suitable is the one having the acid radicle of lowest cross-section for the capture of thermal neutrons. The nitrates and bromides are particularly suitable since bromine, nitrogen, and oxygen nuclei have negligible capture cross-sections for thermal neutrons. Unfortunately the nitrates and bromides needed in this investigation are so highly deliquescent that the accurate weighings needed to determine numbers of nuclei could not be made. This difficulty was overcome by using carbonates that could be obtained pure as well as dry, and, after weighings were completed, by converting the carbonates into bromides. Also, in certain cases the elements used included isotopes of unequal but known abundance ratios, the large absorption for thermal neutrons being due to one particular isotope. In such cases due allowance for the abundance ratios were made, and the capture cross-sections were assigned to the particular isotope known to be responsible. The question of purity of the salts used is also of great importance, as a mere trace of an element having a large capture cross-section would seriously affect the results. Actually the usefulness of the solution method is practically limited to the study of nuclei having capture cross-sections that are large compared to those of their associated acid radicles or of the constituents of water itself, and to the use of salts either pure or known to include no trace of an element possessing a large nuclear capture cross-section. In dealing with the problems mentioned in this paragraph the authors found the table prepared by Bethe (3) most useful.

Results

The final determinations of relative capture cross-sections may be made analytically, or graphically as outlined above in the discussion of the theory. The graphical method was employed and involved plotting $1/a$ against N_{Cs} first for aqueous solutions containing cadmium only. Fig. 3 represents a typical series of measurements and shows that the resulting curve is a straight line, as predicted from the theory, and also gives the ranges of concentrations found most suitable. Each point shown represents the result of a group of measurements. A repetition of the series of measurements say on the fol-

lowing day would give likewise a straight line—see dotted line—but with a greater slope due to the decay of the radon. Whatever the strength of the source, such lines should pass through the point P , since OP represents the concentration of cadmium nuclei that offers the same total capture cross-section as the water itself, assuming no other losses. The mean value of OP , obtained from a number of series of observations, was $-12.02 \times 10^{18}/\text{cc.}$

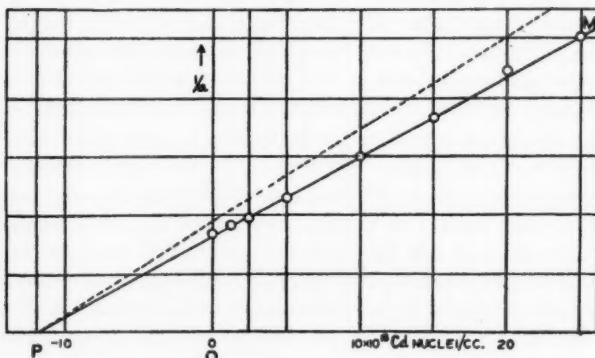


FIG. 3. Curve showing relation between activity of detector and concentration of cadmium nuclei.

The capture cross-section for thermal neutrons of a cadmium nucleus given by Bethe (3) was assumed as correct and to have the value of $2600 \times 10^{-24}\text{cm.}^2$. Since the number of hydrogen nuclei per cubic centimetre is 0.673×10^{23} , the capture cross-section for thermal neutrons for hydrogen may be directly computed on the basis of these values by means of the relation:

$$\sigma_H = \frac{-N_{\text{Cd}(H)} \sigma_{\text{Cd}}}{N_H}$$

The result is $0.464 \times 10^{-24}\text{cm.}^2$. In this it is assumed that any captures by oxygen nuclei and diffusion effects may be neglected. The value obtained is much higher than the value $0.33 \times 10^{-24}\text{cm.}^2$, which was given by Knauer. It is not easy to account for such a large discrepancy on the basis of diffusion losses, since the use of twin sources in the present experiments must have very greatly reduced such losses. Certainly the value obtained must mark the upper limit for σ_H . The uses of stronger sources in the present investigation and an ionization chamber in place of a Geiger counter were other very distinct advantages as thereby the uncertainties due to the background count were reduced. The close agreement in the results of the independent trials herein reported would seem to be significant.

At this point it may be well to report that an experimental check on the existence of the plateau of concentration was made by exposing the silver detector at a series of positions on a line joining the two sources, first without, then with cadmium shields. The resulting activations indicated the plateau effect both for thermal and for fast neutrons. The latter is important since

the mean free path for thermal neutrons is only about 1 cm. and the "diffusion length" about 3.5 cm. (7). The concentration of thermal neutrons on the plateau then hinges on the conversion of fast neutrons in the plateau region, hence the one plateau follows from the other. Also it was found experimentally that the concentration of fast neutrons in the plateau region was inappreciably affected by the nature of the solution. This experimental fact greatly supports the theory of this method.

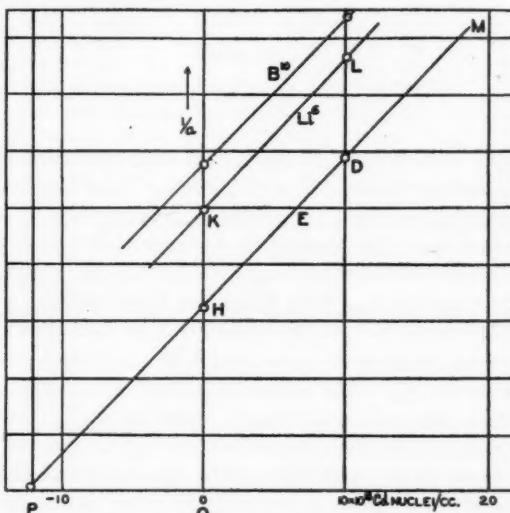


FIG. 4. Curves showing effects of adding other absorbing nuclei to solutions containing cadmium nuclei on the induced radioactivity of the detector.

The method employed in the determination of the capture cross-sections for thermal neutrons for other nuclei may be readily understood from the curves shown in Fig. 4. PM represents the line passing through the point -12.02×10^{18} and points H and D which were obtained respectively with water alone and with a cadmium solution containing 10×10^{18} Cd nuclei per cc. Points K and L represent values obtained when to the water and to this cadmium solution enough lithium bromide was added to give each a Li^6 nuclei concentration of 21.22×10^{18} . This required a total of 268.6×10^{18} ordinary lithium nuclei per cc. since the abundance ratio of Li^6 is 7.9% (8). It is seen that the addition of the lithium has increased the intercept by an amount equivalent to KE . This was found to have a mean value of 6.91×10^{18} . Since the capture of slow neutrons by the lithium nuclei has been found due to the Li^6 isotope, the value of σ_{Li^6} is given by the relation:

$$\sigma_{\text{Li}^6} = \frac{-N_{\text{Cd}(\text{Li}^6)}\sigma_{\text{Cd}}}{N_{\text{Li}^6}}$$

A substitution of the above values leads to $846 \times 10^{-24} \text{ cm.}^2$ as the value of σ_{Li^6} .

In a similar manner other capture cross-sections were measured. Table I gives the values obtained, together with the values listed by Bethe (3) in his summary.

TABLE I
VALUES OF σ_{capture} OBSERVED, AND VALUES PREVIOUSLY PUBLISHED

Nucleus	σ_{capture} (Observed)	σ_{capture} (Bethe)
Cd	$2600 \times 10^{-24} \text{cm.}^2$ (assumed)	$2600 \times 10^{-24} \text{cm.}^2$
B ¹⁰	$2760 \times 10^{-24} \text{cm.}^2$	$3000 \times 10^{-24} \text{cm.}^2$
Li ⁶	$846 \times 10^{-24} \text{cm.}^2$	$900 \times 10^{-24} \text{cm.}^2$
Hg	$323 \times 10^{-24} \text{cm.}^2$	$440 \times 10^{-24} \text{cm.}^2$
Ba	Less than $21.4 \times 10^{-24} \text{cm.}^2$ (See below)	$140 \times 10^{-24} \text{cm.}^2$

It is of interest to note that the agreement with published values is reasonably close in each case, except that of barium, if the uncertainties involved in the experimental methods employed previously are considered. It is generally believed that the absorption by cadmium nuclei is due entirely to capture, hence the cadmium nucleus was a suitable one to take as a standard. Since each other value for σ_{capture} falls below the corresponding value in Bethe's table, it might be suspected that the value given for cadmium itself is too low.

The experimental work in the cases of Li⁶, B¹⁰, and Hg involve a statistical error of the order of 2%. The extent to which the results may be affected by any absorption due to bromine nuclei must be small. Any uncertainties as to whether, when water alone is used, there may be losses of neutrons other than through captures by hydrogen nuclei as mentioned above, are not involved here, as water is present in each of these cases, and such effects would be constant. Certainly the method is simple and the comparisons direct. Should the value of σ_{capture} assumed correct in this investigation be found later to require revision, the values herein listed would be affected accordingly.

These results with barium were quite unexpected and interesting. Neglecting the absorption of the associated bromine nuclei and following the same technique as for the other nuclei, the capture cross-section was found to be $21.4 \times 10^{-24} \text{cm.}^2$, in strong disagreement with the previously published value of $140 \times 10^{-24} \text{cm.}^2$. In view of this result a new determination using barium from a different stock was carried out, but the result obtained was in excellent agreement with that of the first determination. If the value given by Bethe for the bromine nucleus is accepted, then the two bromine nuclei associated with the barium atom would fully account for the observed captures, and it might well be concluded that the barium nucleus has a negligible capture cross-section for thermal neutrons.

While the above report was in the hands of a referee, a paper reporting the same type of work was published by Lapointe and Rasetti (see Phys. Review, 58, 554. 1940). While the experimental approach and the elements tested were for the most part different, it is interesting to note that these observers,

too, found the capture cross-section of the barium nucleus to be very small. They, like the present authors, experimentally proved that the density of the fast neutrons in the region of the detector is inappreciably affected by the nature of the solution.

Acknowledgment

The authors are grateful to the Saskatchewan Cancer Commission for the radon used in this investigation. Having the plant located at the University was highly advantageous in the preparation of the sources.

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THE DIFFUSION OF WATER VAPOUR THROUGH A SLIT IN AN IMPERMEABLE MEMBRANE¹

By J. D. BABBITT²

Abstract

Starting with the elementary equation for the diffusion of a vapour, an equation is developed giving the relation between the amount of vapour diffusing through a slit in an impermeable membrane and the width of the slit. The results given by this equation are compared with experimental values and a satisfactory agreement is obtained.

Introduction

In order to prevent the condensation of moisture in the walls of buildings it has become standard practice to provide in the wall a membrane of some material having vapour barrier qualities. This vapour barrier is placed at such a position that the vapour cannot reach those cold parts of the wall where condensation might occur. Methods have been developed by means of which the value of various materials as vapour barriers can be measured, and data have been obtained on the merits of the different types of construction. It is difficult however to evaluate the effects of cracks or joints in such a vapour barrier membrane, and, since in most cases the vapour barrier cannot be applied to the wall in one unbroken sheet but must be built up from a number of small sections or panels, this is important.

In the majority of constructions some sort of a building paper is used as the vapour barrier. In this case the joints can easily be overlapped, and, if an especially tight seal is desired, asphalt or some other sealing compound can be used to seal the overlap. In constructions of this nature the effect of the cracks can be neglected; in other cases, however, it is impossible to obtain an overlapped joint, and then the cost of obtaining a satisfactory seal is prohibitive. Under these conditions a small slit or crack remains in the otherwise vapour proof membrane and it is important to estimate how this slit will affect the vapour barrier qualities of the construction.

Such a problem was presented to the National Research Laboratories in the course of its work on vapour barriers. In certain types of construction an aluminium-backed building board is used as a plaster base. The aluminium foil not only serves as a vapour barrier but also adds a certain amount to the insulation of the wall. With the increased attention that is being given to vapour barriers, the point was raised that in such a construction it was not practical to seal the cracks between the boards, and the resulting flow of vapour might lead to condensation in the wall. It was, therefore, imperative to determine the amount of vapour diffusing into the wall in this manner.

¹ Manuscript received December 31, 1940.

Contribution from the Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 979.

² Physicist.

in order to compute whether the wall as a whole could be considered as adequately protected from condensation.

In order to attack this problem a series of measurements were made to determine the amount of water vapour diffusing through cracks of different widths under standard conditions. At first sight it might be expected that the amount of water vapour would be directly proportional to the area of the crack. However, preliminary results obtained from the measurements immediately showed that this viewpoint was much too superficial, and that the diffusion through narrow cracks was proportionally much greater than that through wide ones. This follows naturally if it is considered that the lines of flow are not straight lines perpendicular to the crack and that the vapour diffuses in from the side. There is, therefore, a greater flow through the edges of the slit than through the centre. Thus the narrow slits will transmit proportionally a greater amount of vapour than the wide ones.

The importance of this fact from a practical standpoint was such that it warranted a more thorough investigation of the problem. In this paper the theory underlying the diffusion of water vapour through such a crack is developed, and the resulting equation is shown to agree with experimental measurements.

Development of Theory

The theory underlying the diffusion of a vapour was first developed by Stefan (4) who was primarily interested in the evaporation from a circular beaker. He pointed out the essential difference between the evaporation or condensation of a vapour and the inter-diffusion of two non-condensing gases. In the case of the two non-condensing gases, the fluxes of partial pressure across any plane perpendicular to the direction of diffusion are opposite and equal for the two gases. This follows from the fact that the total pressure must everywhere be equal so that if Gas A is diffusing in one direction there must be a corresponding diffusion of Gas B in the opposite direction in order that no inequalities of pressure will be built up. In a case such as this the fundamental equations are (3, p. 370).

$$\rho_1 u_1 = - \frac{k_1 k_2}{CP} \frac{d\rho_1}{dx} \quad \text{and} \quad \rho_2 u_2 = - \frac{k_1 k_2}{CP} \frac{d\rho_2}{dx}, \quad (1)$$

where ρ = density of the gas,

u = velocity of the gas,

$k = \frac{RT}{M}$ = a constant at constant temperature

P = total pressure = $\rho_1 + \rho_2$, where ρ_1 and ρ_2 are the partial pressures,

and C = coefficient of resistance.

The subscripts 1 and 2 refer to Gas A and Gas B respectively. According to Equations (1) the diffusion coefficient, D , is equal to $\frac{k_1 k_2}{CP}$ and is proportional to the reciprocal of the total pressure.

In the case of the condensation or evaporation of a vapour, the condition of equality of the fluxes of partial pressure does not hold, because the fact that the vapour is condensing or evaporating assures that the total pressure remains constant without any movement of the second gas. There is, then, in this case the movement of one gas alone. As Stefan has shown, the equation governing this movement is:

$$\rho_1 u_1 = - \frac{k_1 k_2}{C(P - p_1)} \frac{dp_1}{dx}, \quad (2)$$

which differs from Equations (1) in that the denominator contains $(P - p_1)$ instead of P . Now since $p_1 = k_1 \rho_1$, we can write

$$\rho_1 u_1 = - \frac{k_1}{C(P - p_1)} \frac{dp_1}{dx}$$

In this case let us be assumed, after Stefan, that the coefficient of diffusion $D = \frac{k_1}{C}$, so that

$$\begin{aligned} \rho_1 u_1 &= - \frac{D}{(P - p_1)} \frac{dp_1}{dx} \\ &= D \frac{d}{dx} [\log (P - p_1)] \end{aligned} \quad (3)$$

Put

$$V \equiv \log (P - p_1).$$

Then

$$\rho_1 u_1 = D \frac{dV}{dx}. \quad (4)$$

Now, this equation is similar in form to that giving the relation between the charge on the surface of a conductor and the field at that point ($4\pi\sigma = -D \frac{dV}{dn}$, where σ is the charge per unit area and D is the dielectric constant) and to the equation governing the flow of heat in a solid body ($Q = C \frac{dt}{dx}$, where Q is the amount of heat transmitted across unit area when the temperature gradient is $\frac{dt}{dx}$. C is the coefficient of thermal conductivity). The mathematical theory developed in those cases can be applied to diffusion. It is obvious then that diffusion in three dimensions can be represented by Laplace's equation in the form:

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \quad (5)$$

This is the fundamental equation governing the diffusion of a vapour. It is essential to note that V , the potential function, has the form $\log (P - p_1)$.

It remains now to solve Laplace's equation in this form subject to the boundary conditions pertaining to the problem. It is required to find how the amount of water vapour diffusing through a slit of infinite length in an impermeable material varies with the width of the slit. Since the length of

the slit can be considered infinite, it is only necessary to consider a section of unit length, so that the problem may be reduced to one of two dimensions. Laplace's equation can therefore be used in the form.

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} = 0. \quad (6)$$

In order to obtain a solution of this equation it is necessary to use the method of conjugate functions*.

Put

$$z = x + iy \quad \text{and} \quad W = U + iV, \quad (7)$$

where z and W are complex imaginaries that are connected by the relation $z = \phi(W)$, where $\phi(W)$ is some function of W . Let it be assumed that

$$\phi(W) = f \cos W,$$

where f is a constant whose significance will be determined later. Then

$$\begin{aligned} z &= f \cos W \\ &= f \cos(U + iV) \\ &= f(\cos U \cos iV - \sin U \sin iV) \\ &= f(\cos U \cosh V + i \sin U \sinh V) \end{aligned}$$

By comparing this with Equation (7) the following parametric equations for x and y are obtained:

$$x = f \cos U \cosh V \quad \text{and} \quad y = f \sin U \sinh V \quad (8)$$

Elimination of U and V respectively from these equations gives the relations

$$\frac{x^2}{f^2 \cosh^2 V} + \frac{y^2}{f^2 \sinh^2 V} = 1 \quad (9)$$

and

$$\frac{x^2}{f^2 \cos^2 U} - \frac{y^2}{f^2 \sin^2 U} = 1 \quad (10)$$

Equation (9) is the equation of a family of confocal ellipses whose semi-axes are $f \cosh V$ and $f \sinh V$ respectively, while Equation (10) is the equation of a family of confocal hyperbolas of semi-axes $f \cos U$ and $f \sin U$. f is thus the focal distance in both cases. These curves have been plotted in Fig. 1. It is obvious now from the theory of conjugate functions that V given by Equation (9) can be considered as satisfying the conditions of a potential in Equation (6) and that the confocal ellipses are the equipotential surfaces. On this viewpoint the confocal hyperbolas are the lines of flow at right angles to the equipotential surfaces. When $V = 0$ is substituted in Equation (9), the confocal ellipse becomes a line joining the two foci. This is the case in which we are interested as this line may be considered as a slit through which the vapour is diffusing. We are concerned in finding how the amount of vapour flowing through the slit varies with the width of the slit, that is, with the focal distance.

* See, for instance: J. H. Jeans, "Electricity and Magnetism", Cambridge Press, 1927, p. 270; Handbuch der Physik, Band XII, p. 472; Clerk Maxwell, "Electricity and Magnetism", Oxford Press, 3rd ed. 1901, Vol. I, p. 296.

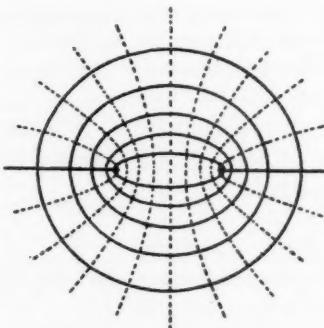


FIG. 1. Potential surfaces and lines of flow through slit.

In order to proceed with this it simplifies matters if the corresponding electrostatic problem is considered. This would be the case of an infinite strip of conducting material embedded in a non-conducting medium. The non-conducting medium will be considered to be a vacuum, so that the dielectric constant will be equal to unity. Then

$$4\pi\sigma = - \frac{\partial U}{\partial s} \quad (11)$$

where σ is the charge per unit area and ∂s is a small element of surface.

Now in this system of confocal ellipses

$$ds^2 = dx^2 + dy^2 = f^2 (\cosh^2 V - \cos^2 U)(dU^2 + dV^2).$$

From this it follows that, on the equipotential surfaces where $V = \text{constant}$,

$$\bullet \quad \frac{dU}{ds} = \frac{1}{f\sqrt{\cosh^2 V - \cos^2 U}} = -4\pi\sigma. \quad (12)$$

But the general equation for the charge σ on the surface of an ellipsoid is given by*

$$\sigma = \frac{q}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2}}}, \quad (13)$$

where a , b and c are the axes of the ellipsoid and q is the total charge. In the case of our system of elliptical cylinders, where c is infinite we can write $\frac{q}{2c} = \epsilon$, where ϵ is the charge per unit length. Then

$$4\pi\sigma = \frac{2\epsilon}{ab} \frac{1}{\sqrt{\frac{x^2}{a^2} + \frac{y^2}{b^2}}}$$

and substituting for x and y from Equation (8) and remembering that $a = f \cosh V$ and $b = f \sinh V$ we obtain

$$4\pi\sigma = \frac{2\epsilon}{f^2 \sqrt{\cosh^2 V - \cos^2 U}} \quad (14)$$

* cf. *Handbuch der Physik*, vol. XII, p. 459.

Comparison of this with Equation (12) shows that the charge per unit length of the cylinder is given by

$$e = -\frac{1}{2} \quad (15)$$

This is to say, that the charge on each of the cylinders is equal to $-\frac{1}{2}$. It is essential to realize that this charge distribution is that which is required to build up the potential distribution from which we obtained the equations for the equipotential surfaces. From the derivation it follows that the potential was zero on the line joining the foci and from there it increased to infinity at an infinite distance. Now it is obvious that any of the equipotential surfaces may be raised to any potential desired. In that case the charge e will change accordingly. The invariable quantity connected with the cylinders is the capacity. The capacity can be calculated from the specific case that was used to obtain the equations for the cylinders and then this value of the capacity may be used to calculate the charge that will be necessary to raise the cylinder to the desired potential.

From the above, it is known that $e = \frac{1}{2}$ for any cylinder that may be defined by the relation $\sinh V = \frac{b}{f}$, where b is the minor axis. For the capacity of this cylinder, therefore,

$$\begin{aligned} C &= \frac{e}{V} = \frac{1}{2V} = \frac{1}{2 \sinh^{-1} \frac{b}{f}} \\ &= \frac{1}{2 \log \frac{a+b}{f}} \\ &= \frac{1}{\log \frac{a+b}{a-b}}. \end{aligned} \quad (16)$$

This equation gives the capacity of any of the equipotential cylinders and this depends only on the major and minor axes of the cylinder. Let us see now how we can apply this solution to our specific problem.

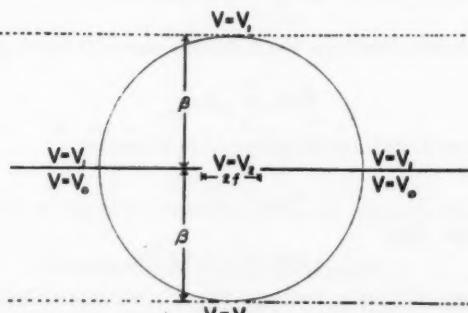


FIG. 2.

At some particular distance β from the slit (see Fig. 2) there is a potential $V = V_1$ [corresponding to $V_1 = \log(P - p_1)$], while at the slit there is a potential $V = V_2$ [corresponding to $V_2 = \log(P - p_2)$, where p_2 is the vapour pressure at the slit]. Also it can be assumed that at a distance β on the other side of the slit the pressure is p_0 , so that $V = V_0 = \log(P - p_0)$. For the time being conditions on the under side of the slit can be neglected, since it is obvious that these will be the exact converse of those on the upper side.

We are interested then in the capacity of a system composed of an elliptical cylinder of minor axis β and the line joining its foci. Employing the same reasoning that was used to obtain Equation (16), we find the capacity of the two confocal elliptical cylinders to be

$$C = \frac{e}{V_1 - V_2} = \frac{1}{2 \log \frac{a_1 + b_1}{a_2 + b_2}}. \quad (17)$$

In the case of the two cylinders in which we are interested,

$$\begin{aligned} b_1 &= \beta \\ a_1 &= \sqrt{\beta^2 + f^2} \\ b_2 &= 0 \end{aligned}$$

and

$$a_2 = f.$$

Thus the capacity of the system is given by

$$C = \frac{1}{2 \log \frac{\sqrt{\beta^2 + f^2} + \beta}{f}}. \quad (18)$$

This refers to the complete cylinder. For the present we are interested in only the upper half so that the capacity would be one-half of the above. Thus

$$C = \frac{1}{4 \log \frac{\sqrt{\beta^2 + f^2} + \beta}{f}}. \quad (19)$$

It is necessary now to find how the diffusion case is related to the electrostatic. In the latter,

$$4\pi\sigma = - \frac{dV}{dn}, \quad (20)$$

while for the former we have developed the equation

$$\rho_1 u_1 = D \frac{dV}{dn}. \quad (21)$$

It is then obvious that

$$\rho_1 u_1 = - 4\pi D\sigma, \quad (22)$$

and that the mass diffusing through the slit is proportional to the charge in the corresponding electrostatic problem. It is obvious that the mass diffusing through unit length would be proportional to the charge per unit length.

The charge per unit length in the system composed of elliptical cylinder and the line joining the foci is

$$\begin{aligned} e' &= C(V_1 - V_2) \\ &= \frac{V_1 - V_2}{4 \log \frac{\sqrt{\beta^2 + f^2} + \beta}{f}}, \end{aligned} \quad (23)$$

and thus from Equation (22) the mass W diffusing through unit length of the slit would be

$$\begin{aligned} W &= \int \rho_1 u_1 ds = -4\pi D f \sigma ds = 4\pi D e' \\ &= -\pi D \frac{V_1 - V_2}{\log \frac{\sqrt{\beta^2 + f^2} + \beta}{f}} \end{aligned} \quad (24)$$

and since

$$\begin{aligned} V_1 &= \log(P - p_1) \quad \text{and} \quad V_2 = \log(P - p_2) \\ W &= -\pi D \frac{\log \frac{P - p_1}{P - p_2}}{\log \frac{\sqrt{\beta^2 + f^2} + \beta}{f}}. \end{aligned} \quad (25)$$

This then gives the essential equation relating the mass of vapour diffusing through the slit with the half-width of the slit f .

There are two simplifications that can be made in this formula. In the first place β is, by hypothesis, large compared with f , so that f^2 may be neglected in comparison with β^2 . Secondly in order to apply the formula it is generally simpler to consider the vapour as diffusing from a vapour pressure p_1 at a distance β above the slit to a pressure p_0 at the distance β below the slit. From a consideration of symmetry the potential at the slit will be half-way between the potential at β and $-\beta$. Thus

$$\begin{aligned} V_1 - V_2 &= \frac{1}{2}(V_1 - V_0) \\ &= \frac{1}{2}[\log(P - p_1) - \log(P - p_0)] \\ &= \frac{1}{2} \log \frac{P - p_1}{P - p_0}. \end{aligned} \quad (26)$$

Hence

$$W = -\frac{\pi D}{2} \frac{\log \frac{P - p_1}{P - p_0}}{\log \frac{2\beta}{f}}. \quad (27)$$

This is the equation relating the mass diffusing through the slit with the half-width f .

Comparison with Experiment

In order to test Equation (27) two sets of experiments were carried out. In both cases aluminium foil was used as the impermeable membrane. In the first set of experiments this foil was placed between two pieces of plaster-

board each $\frac{1}{8}$ in. thick; in the second set the plasterboard was replaced with two pieces of $\frac{1}{8}$ in. fibreboard. This experimental arrangement was used in preference to a membrane in air alone as it was felt that in the latter case convection currents and currents caused by the fan in the humidity chamber would disturb the potential distribution. The specimens constructed in this way were mounted in glass crystallizing dishes, and the amount of water vapour diffusing through the slit was measured by the method used to obtain the permeability of building materials.

TABLE I
ALUMINIUM FOIL BETWEEN TWO PIECES OF PLASTERBOARD

Width of slit $2f$, cm.	Transmission, gm./24 hr./cm.	Width of slit $2f$, cm.	Transmission, gm./24 hr./cm.
0.022	3.64×10^{-3}	0.182	6.14×10^{-3}
0.042	4.36	0.260	7.97
0.072	5.00	0.374	7.43
0.113	5.54		

TABLE II
ALUMINIUM FOIL BETWEEN TWO PIECES OF FIBREBOARD

Sample	Width of slit = $2f$, cm.	Transmission, gm./24 hr./cm.	Sample	Width of slit = $2f$, cm.	Transmission, gm./24 hr./cm.
I	0.009	5.24×10^{-3}	II	0.075	7.37×10^{-3}
I	0.048	7.01	II	0.106	7.44
I	0.086	7.34	II	0.153	7.89
I	0.115	7.26	II	0.208	8.55
I	0.142	7.40	II	0.315	10.72
I	0.166	8.41	II	0.382	9.35
I	0.219	9.28	III	0.024	5.42
I	0.305	9.08	III	0.130	6.90
I	0.394	12.02	IV	0.018	5.14
II	0.047	6.84			

The results of the measurements are given in Tables I and II. In these experiments the temperature was 89.8° F. and the external relative humidity was maintained at 75%. Hence the vapour pressure difference across the samples was 26.6 mm. of mercury.

Now consider Equation (27)

$$W = -\frac{\pi D}{2} \frac{\log \frac{P - p_1}{P - p_0}}{\log \frac{2\beta}{f}}.$$

Since in all the measurements the vapour pressures were the same, $\log \frac{P - p_1}{P - p_0}$ can be considered as constant and the equation can be written in the form

$$W = \frac{C_1}{C_2 - \log 2f}, \quad (28)$$

where

$$C_1 = -\frac{\pi D}{2} \log \frac{P - p_1}{P - p_0}$$

and

$$C_2 = \log 2\beta + \log 2.$$

If, therefore, $\log 2f$ is plotted against $\frac{1}{W}$ the resulting curve will be a straight line. The slope of this line will give the constant C_1 , from which D can be determined since $\log \frac{P - p_1}{P - p_0}$ can be evaluated. C_2 and hence β can be determined from the fact that the intercept on the $\frac{1}{W}$ -axis is equal to C_2/C_1 .

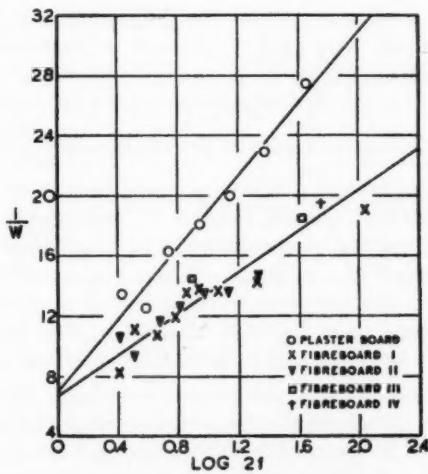


FIG. 3. Relation between $\frac{1}{W}$ and $\log 2f$.

In Fig. 3, $\frac{1}{W}$ has been plotted against $\log 2f$ for the two sets of samples. From these curves the following data are obtained for the plasterboard and fibreboard samples respectively:

(1) *Plasterboard:*

$$C_2/C_1 = 7.00$$

thus

$$C_1 = 0.0837,$$

$$C_2 = 0.586.$$

From this it is found that $D = 3.44$ gm./24 hr./sq. cm./unit change in $\log (P - p_1)$ and

$$\beta = 0.96 \text{ cm.}$$

It is interesting to compare these values with those obtained from other measurements. In the ordinary measurement of diffusion coefficients (1, 2) the less accurate formula

$$W = -d \frac{dp}{dx}$$

is used. This corresponds to Equation (1). Comparing this with Equation (3) it is seen that

$$d = \frac{D}{P - p_1}.$$

The error involved in using this simpler formula instead of the more accurate log formula is small for the range of pressures involved in our work. Therefore by changing D to the usual unit used in permeability measurements it is found that

$$D = 46.9 \text{ gm./24 hr./sq. m./} \frac{\text{mm. Hg}}{\text{cm.}}$$

The value found previously (1) for the diffusance of a plasterboard sample of thickness 0.94 cm. was 22.8. Although a plasterboard of this nature cannot be considered as homogeneous, being faced on each surface with paper, a rough value for D is obtained by multiplying the diffusance by the thickness.

In this way the value 21.4 gm./24 hr./sq. m./ $\frac{\text{mm. Hg}}{\text{cm.}}$ is obtained. In a

more recent publication (2) it has been found that in measuring the permeability of materials such as this there is an appreciable end effect, so that one should expect the true permeability to be larger than the value obtained from a sample only 0.94 cm. thick. When it is considered also that there would be a small air film between the two pieces of plasterboard since no effort was made to cement them together, the value obtained for D from these measurements may be considered to be in good agreement with previous work.

The value obtained for β is also very interesting. Theoretically β is that distance from the slit at which the pressure becomes equal to the exterior pressure. It would be assumed from the experimental set-up that this would approximate to the thickness of the plasterboard. The actual thickness of the latter is 1.05 cm. The fact that β comes out as 0.96 cm. is very satisfactory.

(2) Fibreboard

$$C_1/C_2 = 6.75$$

$$C_1 = 0.146,$$

thus

$$C_2 = 0.988$$

From these values it is found that $D = 6.014 \text{ gm./24 hr./sq. cm./unit change in } \log(P - p_1) \text{ per cm.}$

$$\beta = 2.43 \text{ cm.}$$

If D is changed to the other units as for the plasterboard

$$D = 82.0 \text{ gm./24 hr./sq. m./} \frac{\text{mm. Hg}}{\text{cm.}}$$

A representative value for D taken from the data in (2) would be in the neighbourhood of 50.0. While this is not good agreement, it is of the right order, and the difference could easily be accounted for by the experimental set-up and errors of observation. The thickness of the fibreboard used was 1.3 cm., so that the agreement with β is not so good as was the case with the plasterboard.

In Fig. 4 the curves obtained by substituting the above values for C_1 and C_2 in Formula (28) have been plotted. The experimental values from Tables I and II are also given, and the agreement between the curve and the experimental points is quite satisfactory.

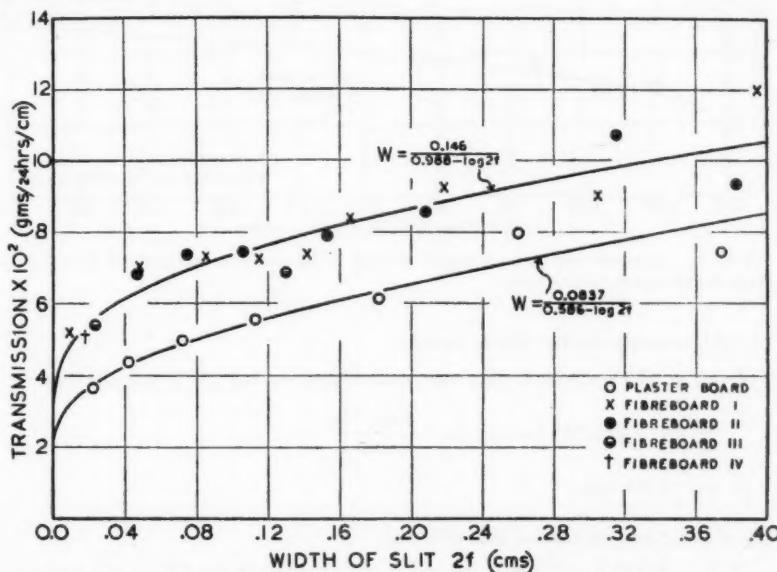


FIG. 4. Transmission of water vapour through a slit cut in aluminium foil enclosed on both surfaces.

Finally, in Fig. 5 are given the results obtained from the original measurements on foil-backed plasterboard. In making these measurements, the plasterboard was placed over the mouth of the cell with the aluminium foil facing outwards. The foil and hence the slit were left exposed to the air in the humidity chamber, which was circulating fairly rapidly owing to the circulating fan. Under these circumstances, it is difficult to say just what D and β mean, but it is obvious from the figure that the experimental results can be explained by an equation such as (27). Measurements were carried out on samples of both the plain aluminium-backed plasterboard samples and on samples that were plastered with $\frac{1}{8}$ in. rough base and $\frac{1}{16}$ in. finishing coat. The values of D and β that are used to plot the curves in Fig. 5 are as follows:

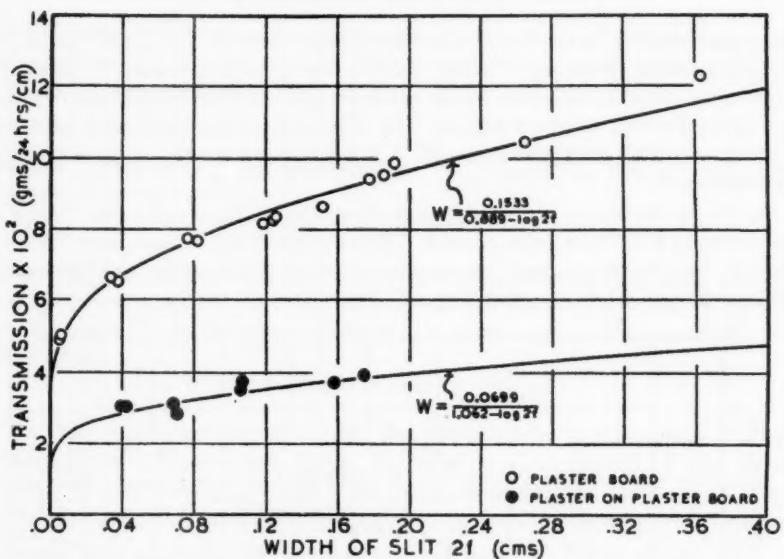


FIG. 5. Transmission of water vapour through a slit cut in aluminium foil backed with plasterboard on one surface only.

(1) Aluminium-backed plasterboard:

$D = 6.175 \text{ gm./24 hr./sq. cm. unit change in } \log(P - p_i) \text{ per cm.}$

$$= 84.3 \text{ gm./24 hr./sq. m./} \frac{\text{mm. Hg}}{\text{cm.}}$$

$$\beta = 1.94 \text{ cm.}$$

(2) Plaster on foil-backed plasterboard:

$$D = 3.370 \text{ gm./24 hr./sq. cm./ unit change in } \log(P - p_1) \text{ per cm.}$$

$$= 45.7 \text{ gm./24 hr./sq. m./} \frac{\text{mm. Hg}}{\text{cm.}}$$

$$\beta = 2.88 \text{ cm.}$$

These results have been given in order that they may be available for calculations involving the amount of vapour diffusing through such cracks in actual construction. It is essential therefore to state that the vapour pressure differences in the two sets of experiments were 27.1 and 22.8 mm. of mercury for the plasterboard and the plastered plasterboard respectively. Therefore in order to obtain the amount of vapour diffusing through the slit per unit vapour pressure, the transmissions obtained from the curves must be divided by 732.9 and 737.2 respectively. The results will then be given in grams per 24 hours per millimetre of mercury per centimetre length of crack.

Acknowledgment

The author wishes to express his appreciation of the work of W. A. Rowe, laboratory helper at the National Research Laboratories, who carried out the numerous weighings involved in the measurement of the vapour transmissions. He also wishes to acknowledge the suggestions which he gained from Dr. C. D. Niven in many discussions of this problem.

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Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 19, SEC. B.¹

MARCH, 1941

NUMBER 3

THERMAL STUDIES ON ASBESTOS

III. EFFECT OF HEAT ON THE BREAKING STRENGTH OF ASBESTOS CLOTH CONTAINING COTTON¹

By D. WOLOCHOW²

Abstract

Commercial, Underwriters', and A grades of asbestos cloth begin to lose strength as soon as heat is applied. On heating for five minutes at 300° C. these three grades of asbestos cloth lose approximately 60, 35, and 25% of their original (conditioned) breaking strength, respectively. Charts are given showing the effect of heating, at temperatures up to 600° C., for periods up to one hour.

Supplementing the study of the effect of heat on the breaking strength of pure or Grade AAAA asbestos tape, which was the subject of the previous paper (1), there is now presented a summary of the results of similar tests on asbestos cloth that contains cotton.

Materials Tested

The samples of cloth tested fall into three grades: Commercial, Underwriters', and A grade. Several samples of each grade were studied, the average asbestos content of the samples in each grade being 79.5, 82.0, and 89.0%, respectively.

The samples had thicknesses ranging from 0.140 to 0.250 in., and weights of 1.5 to 2.5 lb. per yard.

Methods of Test

The samples were conditioned at 70° E., and 65% relative humidity, and the thickness, weight, and breaking strength determined. Strips, about 1½ in. wide and 6 in. long, were then prepared and at least 10 strips were taken for each heating test. After being heated in a well ventilated furnace, the samples were cooled in a desiccator and broken in a machine equipped with standard 1-in. jaws.

Results

The results of the tests are shown in Figs. 1 to 3, in which the percentage of the original breaking strength retained after heating at the temperatures indicated has been plotted against the time of heating. The values are averages for all samples within each grade.

¹ Manuscript received September 16, 1940.
Contribution from Division of Chemistry, National Research Laboratories, Ottawa.
Issued as N.R.C. No. 972.

² Chemist, Division of Chemistry.

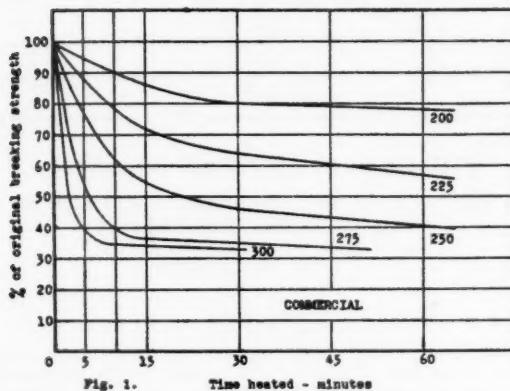


Fig. 1. Time heated - minutes

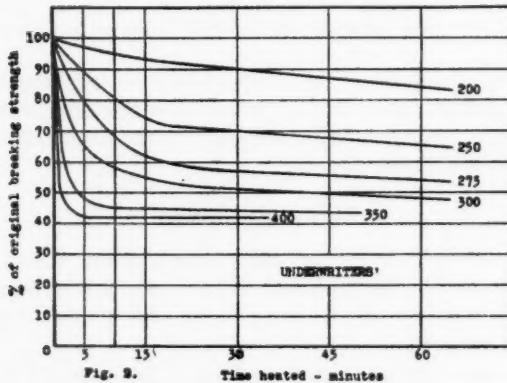


Fig. 2. Time heated - minutes

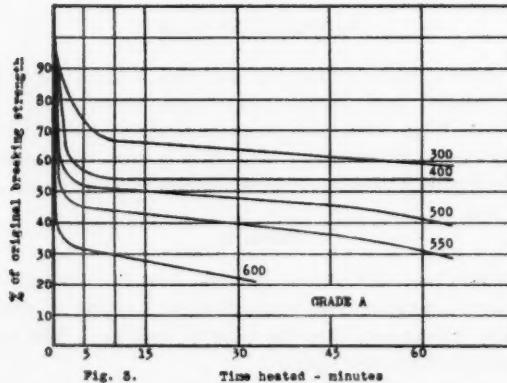


Fig. 3. Time heated - minutes

- FIG. 1. Breaking strength of commercial grade asbestos cloth after heating at 200-300° C.
 FIG. 2. Breaking strength of underwriters' grade asbestos cloth after heating at 200-400° C.
 FIG. 3. Breaking strength of Grade A asbestos cloth after heating at 300-600° C.

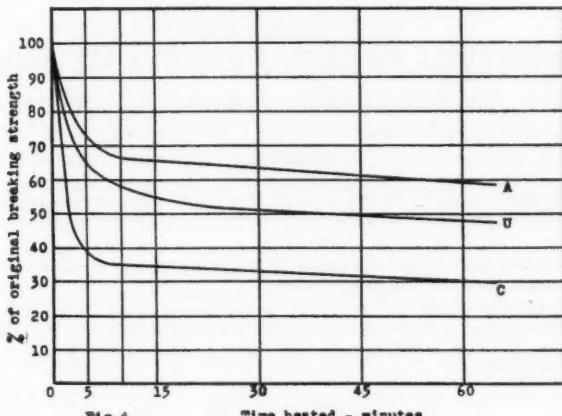


Fig. 4.

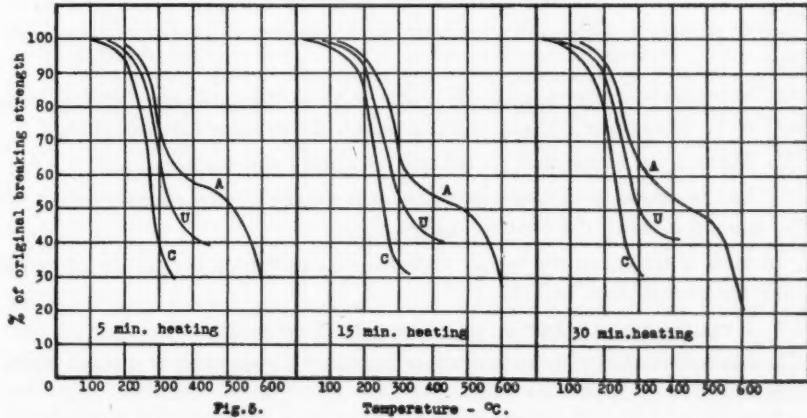


FIG. 4. Breaking strength of commercial, underwriters' and A grades of asbestos cloth after heating at 300° C.

FIG. 5. Breaking strength of commercial, underwriters' and A grades of asbestos cloth after heating for 5, 15, and 30 minutes.

The effect of heating the three grades of cloth at 300° C. is shown in Fig. 4.

In Fig. 5 the percentage of the original breaking strength retained by the three grades of cloth, after heating for 5, 15, and 30 min. has been plotted against the temperature of heating.

From these curves it is possible to predict with a fair degree of accuracy the percentage of the original (conditioned) breaking strength that is retained by Commercial, Underwriters', and A grades of asbestos cloth when heated up to temperatures of 300, 400, and 600°, respectively.

Reference

1. WOLOCHOW, D. Can. J. Research, B, 19 : 56-60. 1941.

THE ANALYTICAL PROBLEM OF MAPLE SAP PRODUCTS¹

BY PAUL RIOU² AND JOACHIM DELORME³

Abstract

A systematic study of official methods of analysis of maple sap products has been made in order to investigate their validity as criteria of the purity of these products.

A new value, the manganese number, is being proposed as a safer criterion but, in some cases, even this may lead to error.

The conclusion of the writers is that, at the present time, it cannot be stated with certainty that a maple product is 100% pure; it is therefore necessary that research work be continued in order to find a criterion of purity that would be valid in every case.

Introduction

As a result of previous investigations involving a study of the manganese content of maple, beet, and cane sugars, the writers came to the conclusion that:

1. Manganese is present in all maple sugars, the amounts ranging from 0.75 to 17.50 mg. per 100 gm. (on dry basis), the average being 5.21 mg.
2. There is no manganese in refined beet and cane sugars.
3. In the majority of cases, manganese is absent in raw sugars, from beet and cane; if present, the content is very low.

In view of these results, certain conclusions concerning the purity of maple products were drawn, i.e., that:

1. A maple sugar containing no manganese is artificial.
2. A maple sugar with a manganese number* higher than 6 is likely to be pure.
3. If the manganese number* is lower than 6, a complete analysis of the product is required to ascertain a possible adulteration.

Since determination of the manganese number provides a test that is rapid and as reliable (or more so) than the usual methods,** the authors propose it as a criterion of the purity of maple sap products. In the present paper, a systematic study of all values used as criteria is made to determine its suitability.

¹ Manuscript received in original form, October 15, 1940, and as revised, December 20, 1940.
Contribution from the Department of Chemistry, Faculty of Commerce, University of Montreal, Montreal, P.Q.

² Professor of Technology, Chairman of the Scientific Research Bureau of the Province of Quebec.

³ Professor of Chemistry and Physics.

* The manganese number is the quantity of manganese in milligrams per 100 gm. of sugar on dry basis.

** For a review of these methods, see (1).

Preliminary Work

In 1936, a determination of the Canadian Lead Number (1, 4) of 22 raw cane sugars was made; the results are given in Table I. It will be noticed that 12 of these (Samples 1-11, 17) have a Lead Value within the range of that for pure maple products. It is evident, therefore, that this value alone cannot be used as a criterion for determining the purity of a maple product (because it does not reveal adulteration with raw sugars).

TABLE I
CANADIAN LEAD NUMBER OF RAW CANE SUGARS

No.	Sample	Value	No.	Sample	Value
1	West Ind. 113	7.40	12	West Ind. 121	12.45
2	Cuba 1a	5.82	13	Cuba 2740	12.48
3	West Ind. 134	5.58	14	Java 5209	10.17
4	Jamaica 1272	5.33	15	Java 5206	9.01
5	Jamaica 2471	4.30	16	West Ind. 8299	8.04
6	Natal (Afr.) 9760	4.03	17	Australia 9749	1.88
7	West Ind. 114	3.47	18	West Ind. 4612	1.63
8	West Ind. 4	3.46	19	West Ind. 121	1.50
9	Jamaica 5	3.23	20	Cuba 3	1.50
10	Trinidad 2472	2.20	21	West Ind. 6	1.48
11	Trinidad 116	2.15	22	Java 5205	1.38

Experimental

In view of the results of the preliminary work, 20 different samples of adulterated products were prepared and, in each, the following values were determined: (a) total ash; (b) soluble ash; (c) insoluble ash; (d) ratio of soluble to insoluble ash; (e) alkalinity of total ash; (f) alkalinity of soluble ash (g) alkalinity of insoluble ash; (h) ratio alkalinity soluble/alkalinity insoluble ash; (i) malic acid value (Cowles method); (j) Canadian Lead Number; (k) conductivity value; (l) manganese number.

Table II lists the different samples prepared and analyzed.

TABLE II
COMPOSITION OF SAMPLES

Sample		Sample	
A	50% Raw cane sugar, "c"-134 50% Raw beet sugar Chatam- "b"	E	50% Raw cane sugar "c"-118 50% Maple sugar (Shefford)
B	50% Raw cane sugar "c"-120 50% Raw beet sugar Chatam- "c"	F	50% Raw cane sugar "c"-119 50% Maple sugar (Gaspé)
C	50% Raw cane sugar "c"-130 50% Raw beet sugar Chatam- "a"	G	50% Raw cane sugar "c"-120 50% Maple sugar (Rigaud)
D	50% Raw beet sugar Chatam- "b" 50% Maple sugar (St. Vincent)	H	50% Raw beet sugar "b"-3118 50% Maple sugar (Quebec)

TABLE II—*Concluded*
COMPOSITION OF SAMPLES—*Concluded*

Sample		Sample	
I	50% Raw beet sugar "b"—55035 50% Maple sugar (Sutton)	C-120	100% Raw cane sugar
J	50% Raw cane sugar "c"—132 50% Maple sugar (Nominingué)	C-130	100% Raw cane sugar
K	50% Raw cane sugar "c"—134 50% Maple sugar (Beauce)	C-132	100% Raw cane sugar
L	50% Raw cane sugar "c"—130 50% Maple sugar (Nominingué)	C-134	100% Raw cane sugar
C-118	100% Raw cane sugar	B-3118	100% Raw beet sugar
C-119	100% Raw cane sugar	B-55035	100% Raw beet sugar

Results

In Table III are given the analytical values found in the adulterated products and the minimum and maximum for corresponding values in pure maple products.

Discussion

A comparison of the analytical values found in adulterated maple products with those of pure products (Table III) show that, in numerous cases, e.g., samples E, C, A, several values were outside the range for pure products and were undoubtedly impure. In others, e.g., samples D, F, L, the only value lying outside the range was the manganese number (less than 6.00) and that alone led to a detection of the adulteration. In two samples (I, K) all values were within the pure product range but the manganese number (6.00), being at the lower limit of the range, suggested a possible adulteration. It is therefore evident that the manganese number is by far a safer criterion of the purity of a maple sap product than any of the other values.

In calculating the number of times the official methods have led to error with respect to the purity of the product, the following figures for each value were found.

Total ash:	80%	Alk. sol. ash:	70%
Soluble ash:	70	Ratio alk. sol./alk. ins. ash:	85
Insol. ash:	80	Malic acid value (Cowles):	45
Ratio sol./insol. ash:	75	Canadian lead number:	65
Alk. total ash:	65	Conductivity value:	65
Alk. insol. ash:	65	Manganese number:	10

TABLE III
COMPARISON OF ANALYTICAL VALUES OF PURE AND ADULTERATED MAPLE PRODUCTS

Values	Pure products*						Adulterated products					
	Min.	Max.	D	F	L	K	E	J	I	H	C	A
Total ash	0.56	1.70	1.18	0.96	0.99	0.76	0.61	0.70	0.92	1.10	1.65	0.71
Soluble ash	0.27	1.23	0.71	0.60	0.70	0.54	0.16	0.36	0.70	0.76	0.96	0.61
Insoluble ash	0.12	1.01	0.47	0.36	0.29	0.45	0.34	0.22	0.34	0.69	0.10	0.10
Ratio sol./insol. ash	0.43	4.07	1.51	1.67	2.41	2.45	0.36	1.06	3.18	2.24	1.25	6.10
Alkalinity-total ash	0.95	2.67	1.46	1.82	1.94	1.11	1.02	1.01	1.33	1.47	1.00	0.87
Alkalinity insol. ash	0.31	2.08	0.74	1.14	0.63	0.73	0.65	0.55	0.55	0.28	0.27	0.27
Alkalinity sol. ash	0.34	1.40	0.72	0.68	1.01	0.48	0.29	0.36	0.78	0.92	0.72	0.60
Ratio alk. sol./alk. insol. ash	0.21	2.29	0.97	0.60	1.09	0.40	0.55	1.42	1.67	2.57	2.57	2.22
Malic acid value (Cowles method)	0.21	1.82	0.40	0.61	0.66	0.38	0.31	0.32	0.23	0.14	0.17	0.17
Canadian lead number	1.74	7.35	2.99	4.82	5.10	3.21	2.77	2.79	3.32	2.85	1.19	2.00
Conductivity value	96.00	230.00	150.73	166.85	139.97	112.38	101.90	107.54	145.20	165.43	162.88	141.82
Manganese number	6.00	17.50	1.00	2.66	2.05	6.00	1.35	0.75	6.00	5.17	0	0
			B	G	C-120	B-3118	B-55035	C-134	C-142	C-130	C-119	C-118
Total ash	0.56	1.70	0.85	1.25	0.77	1.42	1.34	0.55	0.34	0.45	0.47	0.23
Soluble ash	0.27	1.23	0.75	0.68	0.24	0.96	0.84	0.31	0.26	0.13	0.25	0.20
Insoluble ash	0.12	1.01	0.10	0.57	0.53	0.46	0.50	0.24	0.08	0.32	0.21	0.03
Ratio sol./insol. ash	0.43	4.07	7.50	1.19	0.45	2.09	1.68	1.29	3.25	0.41	1.19	6.66
Alkalinity-total ash	0.95	2.67	0.97	1.72	0.60	1.14	1.13	0.68	0.47	0.68	0.50	0.24
Alkalinity insol. ash	0.31	2.08	0.30	1.30	0.46	0.17	0.15	0.22	0.33	0.44	0.34	0.16
Alkalinity sol. ash	0.34	1.40	0.67	0.42	0.14	0.97	0.98	0.46	0.14	0.24	0.16	0.08
Ratio alk. sol./alk. insol. ash	0.21	2.29	2.23	0.32	0.31	5.71	6.53	2.10	0.42	0.55	0.47	0.50
Malic acid value (Cowles method)	0.21	1.82	0.14	0.22	0.13	0.14	0.12	0.19	0.15	0.12	0.11	0.09
Canadian lead number	1.74	7.35	1.81	2.13	2.20	0.90	0.95	2.67	1.68	0.90	0.67	0.76
Conductivity value	96.00	230.00	167.38	91.11	93.79	157.71	152.01	82.06	78.04	65.73	83.30	44.61
Manganese number	6.00	17.50	0	0.50	0	0	0	0.50	0	0	0	0

* Analytical values provided by Dr. J. F. Snell, Macdonald College, Faculty of Agriculture, McGill University.

Conclusion

These investigations lead the writers to the conclusion that the present methods of analysis in evaluating the purity of maple products are far from being safe. This can be explained by the fact that the methods, as those for testing wine, butter, honey, etc., are based upon a range for each value. In many cases, it can be stated that the product has been adulterated, but it can never be stated, on a scientific basis, that the product is 100% pure.

It may be said, in conclusion, that it would be advisable to continue research work on analytical methods of testing maple products until one is found that determines with certainty the purity of the analyzed product. Then only will the problem of analyzing maple products be solved.

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**THE SYSTEM NAPHTHALENE-*p*-NITROPHENOL:
AN EXPERIMENTAL INVESTIGATION OF ALL THE VARIABLES
IN AN EQUATION OF THE FREEZING POINT CURVE¹**

By A. N. CAMPBELL² AND A. J. R. CAMPBELL³

Abstract

With the object of determining the factors responsible for the inapplicability of the ideal equation of the freezing curve,

$$\log_{10} x = Q/R(1/T_0 - 1/T),$$

a number of experimental determinations have been carried out on the system naphthalene-*p*-nitrophenol. These were: (i) specific heat, (ii) heat of fusion, (iii) heat of mixing, (iv) vapour pressure, (v) vapour composition, (vi) density, (vii) surface tension, (viii) viscosity.

The conclusion is arrived at that the discrepancy is due principally to the invalidity of Raoult's law in this case. Since the deviation is positive with respect to both components, it cannot be ascribed to compound formation in solution. Apart from the deviation from Raoult's law, the solution does not exhibit marked abnormality.

The data obtained also permit of the complete, or almost complete, construction of the *p-t-x* model for this system.

Introduction

An ideal equation, connecting the mole fraction with the depression of the freezing point over the whole range of the freezing point curve, has been given at various times (9): $\log_{10} x = Q/R \cdot (1/T_0 - 1/T)$,

in which Q is the molar heat of fusion (as a first approximation) of the solid phase separating, and T_0 the freezing point of pure solid phase, in absolute degrees. The validity of the equation is unrestricted, if the solution be ideal. It results from this equation that if $\log_{10} x$ be plotted against $1/T$ a straight line should be obtained. According to Andrews and Johnston (1) this behaviour is quite frequently found with metallic systems, but in other cases, e.g., organic systems, this straight-line relation is rather rare. This being the case, it becomes of interest to enquire in what manner a given system deviates from the ideal. A lengthy theoretical discussion of this is given by Roozeboom (9). The absence of straight-line behaviour may be summarized as due to:— (i) inconstancy of Q ; (ii) non-obedience to Raoult's law, i.e., the partial pressure does not vary with the mole fraction.

Only if the heat of mixing of the liquid components is zero, and if the heat of fusion is independent of temperature, is it possible to identify Q with the heat of fusion of the pure component separating from the melt. The heat of mixing is not usually zero and, moreover, it varies with concentration. The heat effect in question here is obviously that involved in the introduction of

¹ Manuscript received in original form October 23, 1940, and as revised, January 3, 1941.

Contribution from the Chemistry Department, University of Manitoba, Winnipeg, Man.

² Associate Professor of Chemistry.

³ Wife of the senior author.

a mole of solid component into an infinite quantity of the equilibrium liquid melt. Roozeboom (9) shows how this quantity can be obtained from a knowledge of the heat of fusion and the "differential heat of mixing". The effect of temperature on the heat of fusion over the relatively restricted temperature range of the present equilibrium diagram (39.5°C .) is not likely to be appreciable. Unfortunately, the integration of the above equation assumes a constant value of Q : it is not possible to introduce a variable Q into the equation in the above form. If, however, the heat of mixing is not zero, the ideal equation cannot be expected to apply.

Apart from the above source of deviation, the straight-line relation will also not be followed if Raoult's law is not obeyed. Of the two sources of discrepancy, the latter effect is likely to be much the more important.

The writers chose for investigation the system naphthalene-*p*-nitrophenol, since this is a simple system, showing only a eutectic unaccompanied by compound separation. The equilibrium diagram has been well established by different workers (6, p. 1291; 8). The quantities that are required to be known for the application of the ideal equation are the heats of fusion and the freezing temperatures (taking $\log x$ as the unknown). The writers determined, in addition to these quantities, the heats of mixing and, as a direct investigation of Raoult's law, the vapour pressures of several different mixtures. Since the latter study showed a marked deviation from Raoult's law, the writers were led to investigate the molar volumes, surface tensions, and viscosities of mixtures as a possible measure of their abnormality. There is no necessary connection between non-conformity with thermodynamically ideal behaviour and other physical properties, but the possibility at least exists that this non-conformity might be reflected as a non-adherence to additivity in the case of some other physical properties.

In addition, a few determinations of the composition of the vapour phase were made. The data obtained permit of the construction of the *p-t-x* model (excepting high pressure curves; cf. Roozeboom (9), the whole volume and diagrams at end) or, what amounts to the same thing, the *p-x* and *p-t* sections in addition to the conventional *t-x* diagram.

Experimental and Results

Materials Used

The naphthalene was obtained as pure from the Eastman Kodak Company. The *p*-nitrophenol was a "certified chemical" from British Drug Houses, and had a melting point of $114^{\circ}\text{C}.$ *

Specific Heat of Solid *p*-Nitrophenol

As the heat of fusion was determined by the method of mixtures, it was necessary to know the specific heat of solid *p*-nitrophenol. This was determined by a method previously described (3). The value found was 0.248 ± 0.009 cal. per gm., this being a mean figure for the range $0 - 20^{\circ}\text{C}$.

*All melting points are uncorrected.

Heat of Fusion

This was determined by the method of mixtures. The heats of fusion of pure *p*-nitrophenol and of the eutectic mixture were obtained. About 100 gm. of substance, contained in a glass bulb, was kept in a fused condition in an electrically controlled thermostat at the temperatures of the respective melting points (114° and 73° C. respectively). The bulb, after attaining the temperature of the thermostat, was dropped into a jacketed calorimeter and the corrected temperature rise obtained in the usual way. The heat of fusion of pure *p*-nitrophenol was found to be 41.7 ± 1.0 cal. per gm., and that of the eutectic mixture, 37.0 ± 1.0 cal. per gm.

Heat of Mixing of the Liquid Components

The heat of fusion of the eutectic mixture (25.3% *p*-nitrophenol) calculated by the mixture rule from the heats of fusion of the components is 37.0 cal. per gm., i.e., identical with the experimental value within the limits of experimental error. Since, however, the experimental error is ± 1.0 cal. per gm., this merely means that the heat of mixing has a maximum value of ± 130 cal. per mole for the eutectic mixture. Subsequent direct experiment showed it to be somewhat larger than this and negative in sign.

Since the heat of mixing was small, it became necessary to determine it directly. This was done by introducing a weighed quantity of naphthalene or *p*-nitrophenol (about 100 gm.) into a Dewar flask which served as a calorimeter. This flask carried a Beckmann thermometer, a direct reading thermometer graduated in tenths of a degree, and a heating coil. The Dewar flask was immersed in a thermostat (containing "Paraffinol", a high-boiling, colourless petroleum product) at a temperature of 120° C. The contents of the Dewar flask was stirred with a fine stream of dry air passing through a copper heating coil in the thermostat and through thermometer tubing in the Dewar. A weighed quantity (about 20 gm.) of *p*-nitrophenol or of naphthalene was placed in a large test-tube, carrying a thermometer graduated in tenths of a degree, and kept in the thermostat. When temperature equilibrium was established, the contents of the test-tube was poured into the Dewar flask, and the temperature restored to its original value electrically.

TABLE I
HEAT OF MIXING

Final composition of mixture produced, mole fraction <i>p</i> -nitrophenol	Heat of mixing per mole of mixture, cal.	Final composition of mixture produced, mole fraction <i>p</i> -nitrophenol	Heat of mixing per mole of mixture, cal.
0.159	-200	0.812	-438
0.284	-350	0.657	-690
0.377	-470	0.563	-680
0.450	-560	0.493	-600
0.640	-700		

The results are contained in Table I. The negative sign indicates that heat is absorbed from the surroundings on mixing.

Vapour Pressures

Some of these were determined in a differential apparatus, some in an absolute apparatus. For solutions having vapour pressures greater than half that of pure naphthalene, a differential method is more accurate, for solutions with vapour pressure less than half that of pure naphthalene, and for pure *p*-nitrophenol, an absolute method is preferable. In the differential method, the mixture was placed in one of two flasks and pure naphthalene in the other; both flasks had the same volume and were connected by a U-shaped glass tube. The U-tube was connected by a short horizontal tube to a long vertical glass tube which in turn was connected at its upper end to a Hyvac pump: a manometer in the circuit showed that the pressure on this side was never greater than 10^{-1} mm. The lower limb, which had a length greater than 760 mm., was connected by pressure tubing to a mercury reservoir. All the limbs of the apparatus had a diameter of about 1 cm., to avoid capillary errors. An inverted bell-jar, filled with Paraffinol, which formed the heating bath, was heated electrically, stirred well, and illuminated from behind. It was not thermostatically controlled, measurements being taken with both rising and falling temperature. The great advantage of this simple apparatus is that it permits of the complete removal of dissolved and occluded gas. No traps were necessary in the pumping train since the vapour pressure, even of pure naphthalene, is almost zero at room temperature. The method of working was to exhaust the apparatus at room temperature, with the mercury level below the U-junction, then by raising the mercury to sever connection between the limbs. Heating was then begun and the difference of level in the limbs joining the two flasks measured with a cathetometer. After measurements had been carried to the highest temperature, the mercury was momentarily lowered to permit of the escape of any dissolved air that might have been evolved. Measurements were repeated with falling temperature. The whole process was then repeated until check determinations were obtained.

The method of operating the absolute apparatus, which was used only for pure *p*-nitrophenol and for mixtures containing 89.8% and 95.0% *p*-nitrophenol, was similar, except that pressures were read directly on the limb connecting with the pump, instead of by reference to the known vapour pressure of naphthalene in a second flask. It was found that mixtures rich in *p*-nitrophenol tended to give a small residual pressure at room temperature, after having been heated to a somewhat higher temperature than usual. This is no doubt due to a slow decomposition of the *p*-nitrophenol, which the writers observed to be appreciably rapid above 186° C. Measurements were therefore never taken above 120° except in the case of *p*-nitrophenol itself, where the smallness of the vapour pressure rendered this unavoidable. The results for pure *p*-nitrophenol are expressed in Table II. All figures are corrected for density and vapour pressure of mercury.

TABLE II
VAPOUR PRESSURES OF *p*-NITROPHENOL

Temp., °C.	Press., mm. Hg	Temp., °C.	Press., mm. Hg	Temp., °C.	Press., mm. Hg
120	0.60	130	0.93	142	1.91
146	2.24	149	2.82	150.5	3.17
153	3.47	156	3.81	157	4.27
162	5.63	165	6.92	168	7.59
169	8.71	177	12.62	182	15.2
184	17.4	186	18.7		

As an economy of space, the somewhat extensive tables giving the vapour pressures of mixtures are not presented here, but certain figures are utilised in the discussion.

Vapour Composition

A series of experiments were carried out at 120° C., a temperature at which all mixtures are completely liquid, to determine the composition of the vapour in equilibrium with different liquids. The liquid mixture was contained in a gas-washing bottle in the thermostat and air passed slowly, after purification and drying, through a copper worm in the thermostat, then through the mixture, then through absorption tubes packed with glass wool. Some of the tubes were on the surface of the thermostat and others immersed in ice-water, immediately outside the thermostat. After weighing the absorption tubes, they were extracted with ether, and nitrogen determined by the Kjeldahl method, the usual precautions being taken for presence of a nitro group. The results shown in Table III were obtained.

TABLE III
VAPOUR COMPOSITION

Composition of liquid mixture, % <i>p</i> -nitrophenol	Composition of vapour, % <i>p</i> -nitrophenol
73.0	2.00
89.8	4.32
95.0	12.4

Densities

The densities of liquid *p*-nitrophenol, of liquid naphthalene, and of mixtures of *p*-nitrophenol and naphthalene were determined at 117.3° C. The mixtures were prepared by weighing into stoppered flasks and melting in the thermostat. An Ostwald pyknometer was not used because of the difficulty of adjusting the liquid in the arms when the liquid solidifies immediately above the surface of the thermostat. An ordinary specific gravity bottle was employed. The

TABLE IV
DENSITIES

<i>p</i> -Nitrophenol, %	Mole fraction <i>p</i> -nitrophenol	$d_{4^\circ}^{117.3^\circ}$	Molar volume, cc.	dV	
				Cc.	%
0.00	0.00	0.9554	134.8	—	—
10.09	0.0937	0.9779	132.4	+0.04	+0.03
14.77	0.1376	0.9879	131.1	-0.02	-0.02
21.52	0.2015	1.007	129.3	+0.10	+0.07
27.54	0.2592	1.023	127.9	-0.05	-0.04
44.28	0.4226	1.070	124.0	+0.35	+0.28
48.38	0.4633	1.084	122.7	+0.11	+0.09
59.62	0.5762	1.121	119.8	+0.21	+0.18
66.49	0.6463	1.148	117.9	+0.16	+0.14
79.89	0.7854	1.195	114.4	+0.32	+0.28
89.71	0.8892	1.236	111.5	+0.17	+0.15
100.00	1.0000	1.282	108.4	—	—

results are given in Table IV. The density of *p*-nitrophenol is given by Hewitt and Winmill (4) as 1.2613 at 129.7° and 1.2329 at 162.5° C.

The experimental molecular volumes of liquid mixtures correspond very closely with those calculated from the mixture rule. There is, however, definitely a small expansion of not more than +0.4%, lying presumably, though not necessarily, at 50 mole per cent. Positive deviations from Raoult's law are usually, though not always, accompanied by an expansion in volume (5).

Surface Tension

The surface tension of *p*-nitrophenol and of mixtures was determined at 121° C. by the method of capillary rise, using naphthalene, for which the surface tension is known (International Critical Tables), as calibrating fluid. The capillary bore (0.353 mm.) was also checked by the mercury thread method. The results are given in Table V.

TABLE V
SURFACE TENSION

Composition of mixture, % <i>p</i> -nitrophenol	Mole fraction	Surface tension, dynes/cm.	Mol. surface energy, $\gamma(Mv)^{2/3}$
0.00	0.00	29.3	771
11.8	0.11	29.9	775
25.3	0.24	31.0	788
33.3	0.315	31.8	801
49.8	0.48	33.7	831
62.3	0.60	34.8	842
73.0	0.71	37.7	896
89.8	0.88	41.8	968
95.0	0.93	43.4	995
100.0	1.00	46.3	1053

When surface tension is plotted against composition in mole fraction, a smooth curve is obtained, convex to the axis of composition. A similar type of curve is obtained when molecular surface energy is plotted against mole fraction.

Viscosity

The viscosity at 121° C. was determined in an Ostwald viscometer, using naphthalene as calibrating fluid. The results are expressed in Table VI, which also gives the observed fluidities and those calculated from Bingham's rule (2): $\phi = m\phi_1 + n\phi_2$, where m and n are the volumes of the two liquids in unit volume of the mixture.

TABLE VI
VISCOSITY

Composition of mixture, % <i>p</i> -nitrophenol	Viscosity, centipoises	$\phi_{obs.}$	$\phi_{calc.}$
0.0	0.440*	2.270	—
11.8	0.478	2.090	2.095
25.3	0.600	1.670	1.894
33.3	0.750	1.335	1.761
49.8	1.055	0.946	1.471
62.3	1.350	0.742	0.235
73.0	1.615	0.619	1.011
89.8	2.045	0.489	0.639
100.0	2.560	0.391	—

* International Critical Tables.

When viscosity is plotted against mole fraction, the curve does not deviate greatly from a straight line, but it is still slightly convex to the axis of composition. The fluidities show a very marked deviation from Bingham's rule, the calculated values being much greater than the observed. On the other hand, the deviations from Egner's rule (7, p. 102), $\log \mu = x_1 \log \eta_1 + x_2 \log \eta_2$, are less and occur principally at the naphthalene end of the series.

TABLE VII
DEVIATION FROM EGNER'S RULE

<i>p</i> -nitrophenol, %	$\eta_{obs.}$	$\eta_{calc.}$	Deviation, %
11.8	0.478	0.535	+11.9
25.3	0.600	0.659	+ 9.85
33.3	0.750	0.767	+ 2.3
49.8	1.055	1.026	- 2.8
62.3	1.350	1.266	- 6.2
73.0	1.615	1.536	- 4.9
89.8	2.045	2.07	+ 1.2

Discussion of Results

For purposes of comparison, the equilibrium data of Rheinboldt (8) are reproduced in Table VIII, together with the values of $1000/T$ and of $\log_{10} \cdot 100 N$, as calculated from the ideal equation on the simple assumption that Q is the heat of fusion of pure component. We take as the heat of fusion of naphthalene 35.6 cal. per gm. (International Critical Tables) and as the heat of fusion of *p*-nitrophenol 41.7 cal. per gm. (see Experimental Part). The heat of fusion was also calculated from the experimental values of temperature and mole fraction.

TABLE VIII
EQUILIBRIUM DATA—OBSERVED AND CALCULATED

Mixture No.	Per cent <i>p</i> -nitrophenol	$T, {}^{\circ}\text{Abs.}$	$\frac{1000}{T}$	$N_{\text{exp.}}$	$\log_{10} \cdot 100 N_{\text{exp.}}$	$\log_{10} \cdot 100 N_{\text{calc.}}$	Calc. heat of fusion, cal./gm.
<i>Naphthalene separating</i>							
1	0.00	353.5	2.83	1.00	2.00	2.00	—
2	11.8	250.0	2.86	0.89	1.949	1.972	64.0
3	25.3	346.5	2.89	0.762	1.882	1.943	73.4
<i>Nitrophenol separating</i>							
4	33.3	350	2.855	0.315	1.498	1.663	62.0
5	49.8	358	2.793	0.477	1.679	1.743	52.0
6	62.3	365	2.740	0.604	1.781	1.811	48.4
7	73.0	371	2.695	0.714	1.854	1.868	46.0
8	75.7	372	2.687	0.742	1.870	1.879	43.4
9	89.1	380.5	2.633	0.883	1.946	1.953	47.4
10	100.0	386	2.59	1.000	2.000	2.000	—

When $\log_{10} \cdot 100 N_{\text{exp.}}$ is plotted against $1000/T$ the straight line relation is far from being obeyed, particularly on the *p*-nitrophenol side of the diagram.

Roozeboom (9) has given a graphical method whereby the differential heat of mixing can be obtained from the graph of the heat of mixing plotted against mole fraction of the mixture produced. This has been done in Fig. 1. By drawing tangents at the corresponding concentrations the differential heats of mixing are obtained. It is obvious at once that the differential heat of mixing for naphthalene separating is zero, and that, for *p*-nitrophenol separating, it has a constant value from 0 to about 50 mole per cent *p*-nitrophenol. The true heat effect involved is then obtained as the algebraic sum of the heat of fusion and the differential heat of mixing. These corrected values of Q cannot be introduced into the equation, because the integration of that equation assumed a constant Q , but it is of interest to compare this true, or corrected, heat effect with the simple molar heat of fusion. This has been done in Table IX for the mole fractions used by Rheinboldt.

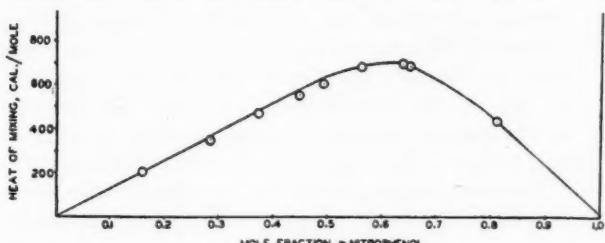
FIG. 1. Relation between molar heat of mixing and mole fraction of *p*-nitrophenol.

TABLE IX
DIFFERENTIAL HEAT OF MIXING

Per cent <i>p</i> -nitrophenol	Corrected heat effect, Cal./mole	Per cent <i>p</i> -nitrophenol	Corrected heat effect, Cal./mole
11.8	-4.56	62.3	-6.52
25.3 } Eutectic	-4.56	73.0	-5.93
25.3	-7.10	75.7	-5.87
33.3	-7.10	89.1	-5.80
49.8	-7.10		

It is apparent from the above that, as far as the heat effect is concerned, the behaviour should be ideal along the naphthalene branch and along the *p*-nitrophenol branch from 100% *p*-nitrophenol to about 73% *p*-nitrophenol, the greatest deviation lying in the range 49.8 to 25.3% *p*-nitrophenol.

In regard to the vapour pressure measurements, when $\log_{10} p$ for pure *p*-nitrophenol is plotted against T in the form of the Clausius-Clapeyron equation, the following equation is obtained for the vapour pressure of liquid *p*-nitrophenol:-

$$\log_{10} p = \frac{-0.05223 \times 76500}{T} + 9.95$$

This equation can be used to calculate the vapour pressure at the melting point, and the temperature of the boiling point ($p = 760$). There is obtained:

$$p_{114^\circ} = 0.396 \text{ mm.}$$

and

$$t_{p=760} = 294^\circ \text{ C.}$$

The literature gives as the boiling point 279° , "with decomposition". Since the writers have found incipient decomposition to begin at 186° , this agreement is as good as could be expected. The vapour pressure up to 100° is low and this is in agreement with the fact that *o*- and *m*-nitrophenols can be separated from *p*-nitrophenol by steam distillation, the *p*-nitrophenol remaining behind.

Knowing the heat of fusion, an equation corresponding to the above can be derived for the sublimation curve. This equation is:-

$$\log_{10} p = \frac{-0.05223 \times 100800}{T} + 13.25$$

By means of these equations, the true partial pressure of the solid component can be determined along the freezing point curve and hence the mole fraction according to Raoult's law ($n' = np$) can be compared with that calculated from the weight composition. This has been done in Table X, in which p' means partial pressure (vapour pressure of solid component) and p the vapour pressure of the pure (supercooled) liquid at the equilibrium temperature. The corresponding equations for naphthalene are taken from the International Critical Tables. They are, for solid naphthalene:—

$$\log_{10} p = \frac{-0.05223 \times 71401}{T} + 11.45,$$

whereas for liquid naphthalene, the data of the International Critical Tables give rise to the following equation:—

$$\log_{10} p = \frac{-0.05223 \times 47700}{T} + 7.946.$$

The mole fraction calculated from Raoult's law ($n = p'/p$) is symbolized n' and that from the weight composition n . The temperatures are taken from Rheinboldt (8)

TABLE X
OBSERVED AND CALCULATED MOLE FRACTIONS

Temp., °C.	p	p'	n'	n
C ₁₀ H ₈ separating { 80.5 77.0	7.954 6.746	7.954 6.31	— 0.937	— 0.882
Eutectic { 73.5 73.5	5.84 0.0252	5.02 0.00892	0.86 0.354	0.747 0.253
<i>p</i> -nitrophenol separating { 77.0 85.0 92.0 98.0 107.5 113.0	0.0355 0.0563 0.100 0.148 0.276 0.399	0.0178 0.0355 0.0708 0.118 0.269 0.399	0.503 0.63 0.708 0.797 0.99 1.000	0.315 0.477 0.604 0.714 0.883 1.000

The values of n' indicate a wide divergence from n . Raoult's law is not obeyed, the divergence being in the sense that both components are more volatile than is calculated from their mole fractions. Such behaviour cannot be accounted for on the basis of compound formation.

The vapour pressure data, in combination with the equilibrium-composition data of Rheinboldt and Kremann, have been utilized to construct Fig. 2, in which, against a common composition axis, are expressed (i) equilibrium temperatures (R and K), (ii) equilibrium pressures, and (iii) composition of the vapour phase. The data of (ii) are obtained from the vapour pressure measurements by a simple interpolation. The data of (iii) are obtained from (ii) knowing the vapour pressure of the solid phase separating. The complete data are assembled in Table XI.

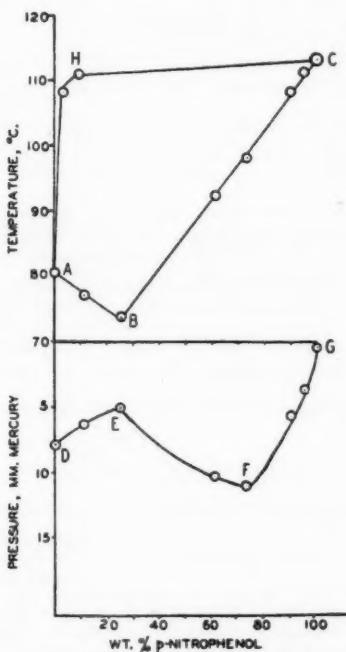


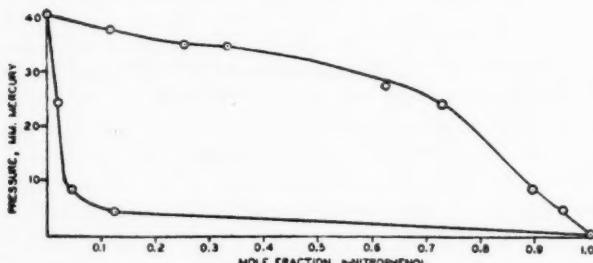
FIG. 2. *ABC*—liquidus. *DEFG*—vapour pressure curve. *AHC*—vapour composition curve.

TABLE XI
EQUILIBRIUM VAPOUR PRESSURE AND COMPOSITION

Per cent <i>p</i> -nitrophenol in liquid	T°, C.	Total pressure, mm.	Weight % <i>p</i> -nitrophenol in vapour
0.0	80.5	7.95	0.00
11.8	77	6.5	—
25.3	73.5	5.1	0.215
62.3	92	10.5	0.687
73.0	98	11.0	1.155
89.8	108	5.75	5.17
95.0	111	3.8	9.85
100.0	113	0.39	100.0

The form of the vapour pressure-composition graph is very uncertain, owing to the fact that an insufficient number of points were determined: the form indicated is a mere suggestion. It is, however, certain that both a maximum and a minimum must occur on the curve.

The vapour pressure figures were now combined with those for vapour composition to obtain Fig. 3. This is an isothermal for 120° C., giving vapour

FIG. 3. Relation between pressure and mole fraction of *p*-nitrophenol.

pressures, total and partial, against liquid composition, as well as vapour composition. The data on which the figure is constructed, together with certain derived quantities, are given in Table XII.

TABLE XII

Composition of liquid, % <i>p</i> -nitrophenol	Total vapour pressure, mm.	Partial pressures		Mole fraction from liquid composition		Mole fraction from partial pressures	
		Naphthalene	<i>p</i> -Nitrophenol	Naphthalene	<i>p</i> -Nitrophenol	Naphthalene	<i>p</i> -Nitrophenol
0.00	40.8	40.8	—	1.00	0.00	1.00	0.00
11.8	37.6	37.4	0.20	0.89	0.11	0.915	0.33
25.3	35.1	34.8	0.30	0.76	0.26	0.85	0.50
33.3	34.7	34.3	0.30	0.68	0.32	0.84	0.50
62.3	27.4	26.9	0.5	0.40	0.60	0.66	0.83
73.0	24.2	23.7	0.5	0.29	0.71	0.58	0.83
89.8	8.5	8.0	0.5	0.12	0.88	0.20	0.83
95.0	4.7	4.1	0.6	0.06	0.94	0.10	1.00
100.0	0.6	0.0	0.6	0.00	1.00	0.00	1.00

The partial pressures are obtained from the vapour composition curve, after conversion to mole fractions. Scrutiny of the two preceding tables reveals that the molar fraction, both for naphthalene and for *p*-nitrophenol, calculated from the Raoult relation is always greater than that calculated from the liquid composition.

As a general summary, it may be said that the principal cause of non-adherence to the ideal equation of the freezing point curve is the deviation from Raoult's law. This deviation from Raoult's law is not, however, accompanied by any very marked abnormality in other physical properties, such as molecular volume, surface tension, and viscosity. It is perhaps connected with the difference in electric moment of the molecules of naphthalene and *p*-nitrophenol, and it is proposed subsequently to investigate this point.

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DETERMINATION OF T.N.T. (2,4,6-TRINITROTOLUENE) IN AIR¹

BY KINGSLEY KAY²

Abstract

A practical method for determining the concentration of T.N.T. in workroom atmospheres has been developed and has been given successful field tests. The accuracy of the method described is approximately $\pm 10\%$. The method is a comparative one, depending upon the red coloration produced when 2,4,6-trinitrotoluene in acetone is treated with a solution of sodium hydroxide in water. The stability of the coloration has been studied and the optimum conditions of temperature and concentrations of reactants have been determined. In addition the range of colour that allows the most accurate comparison has been evaluated. Minor refinements are at present in progress with a view to increasing the accuracy of the test.

Shortly after the beginning of the war, the Division of Industrial Hygiene of the Department of Pensions and National Health, Ottawa, was faced with the problem of supervising health conditions in plants manufacturing and handling T.N.T. (2,4,6-trinitrotoluene). In order that the control of environmental conditions as affecting health might be accomplished, it was necessary to have a means for determining the quantity of T.N.T. in workroom atmospheres. No safe limits for T.N.T. in air were established during the last war, mainly on account of the fact that no satisfactory method for determining this substance in air was developed at that time. This Division, therefore, set about developing a satisfactory method for determining T.N.T. in air that might be available for correlating clinical findings among workers with the concentrations of T.N.T. in the atmospheres in which exposure took place.

A search of the literature disclosed only two investigations in which methods of air analysis for T.N.T. were employed. In 1917, Moore (1) in England, reported analyses of factory air for T.N.T. dust and fumes by a method involving the bubbling of the contaminated air through water. The method required that the air be drawn through water for the full working day and the actual amount of T.N.T. weighed after evaporation of the absorbing liquid. His method gave no indication of the peaks of concentration during the course of a working day and, hence, it was necessary to develop a method of determination that would allow testing of the air over shorter periods, such as one-half to two hours. In connection with this method, it might be pointed out that the efficiency of extraction of T.N.T. from the air was proved by testing the glass tubing on the exit side of the liquid with alcoholic potash. The reaction of T.N.T. with alcoholic potash, which produces a red coloration, was not described. The source of the original observations in this connection has not been found. However, it would appear that this phenomenon was observed at least early in the large-scale production of commercial T.N.T.

¹ Manuscript received January 4, 1941.

Contribution from the Division of Industrial Hygiene, Department of Pensions and National Health, Ottawa, Canada.

² Industrial Hygiene Engineer.

Textbook descriptions of the washing of crude trinitrotoluene point out that attempts were made to wash the acids from T.N.T. with sodium hydroxide, as in the manufacture of nitroglycerine. This proved impracticable, owing to the action of alkali upon T.N.T. which produced dangerously sensitive products of decomposition.

Estimations of T.N.T. in air were also carried out by Phelps and Casselman in the United States and are referred to in a paper by Voegtl, Hooper, and Johnson (2), published in 1922. No description of the method was given and it was not published elsewhere by these investigators.

However, recent communication with the United States Public Health Service has disclosed that Phelps and Casselman investigated two methods, and in addition that similar methods had been described by Elvove under a title "The detection and estimation of certain organic nitro compounds with special reference to the examination of the urine of T.N.T. workers" (J. Ind. Eng. Chem. 11, 861, 1919). The first method, dependent on the action of alkali on T.N.T., is similar to the method described in this paper. However, the present method, while employing a similar reaction, allows accurate detection of quantities of T.N.T. about five times as small. This is an important consideration in lowering air sampling times to suit modern levels of T.N.T. in workroom air.

Method

In the Industrial Hygiene Laboratory of the Department of Pensions and National Health, Ottawa, the reaction of T.N.T. with alkali was studied, with a view to developing it as a method of determination of T.N.T. in air. Crude T.N.T. provided by Canadian Industries, Limited, was purified by precipitation from hot alcohol and acetone, and purity of the 2,4,6-trinitrotoluene recovered was confirmed by melting point determinations. A standard solution of 2,4,6-trinitrotoluene in acetone (0.5000 gm. per 250 cc.) was made up, and the effects of various concentrations and amounts of sodium hydroxide in water and in alcohol on this test solution and dilutions made from it were studied.

Briefly, it was found that addition of 0.1 cc. of a 20% (by weight) solution of sodium hydroxide in water to 1 cc. of a solution of 2,4,6-trinitrotoluene in acetone produced the maximum red coloration in a series of dilutions made from the standard solution. The dilutions were made by adding acetone to the standard in various proportions, and ranged from 1 cc. of the standard in 500 cc. of acetone to 1 cc. of standard in 50 cc. of acetone. The test was conducted by first adding the sodium hydroxide solution to small 1.5 cc. test tubes. Thereafter, the T.N.T. solution was added, the tubes were inverted several times, and allowed to stand. Two phases, of course, were formed, the colour developing at the partition of the phases and migrating into the acetone phase.

The stability of the red coloration was studied and it was found that the colour developed within 10 min. at room temperature and was stable up to

30 min., after which time it gradually faded, leaving the sodium hydroxide phase orange in colour and the acetone phase almost colourless. Stability of the colour product decreased with increase of temperature, and, in the case of heating over a steam bath, the orange decomposition product was formed almost immediately. No investigations were conducted on the chemical constitution of this unstable colour compound. The shade of colour obtained was similar to that of phenolphthalein in solution. It was found that a measurable colour could be developed in acetone solutions of T.N.T. containing as little as 0.000004 gm. per cc.

Experiments were conducted for the purpose of determining the best range of colour over which comparisons might be made with accuracy. It was proved that several different subjects, with the naked eye, could differentiate colour produced in test solutions varying in concentration by $\pm 10\%$ over the range 0.000004 gm. per cc. to 0.00004 gm. per cc. In order to determine the accuracy of the naked eye in comparison of these acetone dilutions of the standard, they were made up in tubes numbered on the bottom. The order of the tubes was destroyed and an attempt made to rearrange them in the correct order. No special efforts were made to standardize the lighting conditions under which the tests were carried out. The tubes were placed in line in a white test tube holder and were viewed in the daylight. In this manner the above-mentioned standard concentrations for colour comparison of unknown concentrations were established.

The accuracy of the method as described above can be regarded as sufficient for the purpose for which the test is required at the present time. Considerable study correlating clinical data with concentrations of T.N.T. in air will be necessary before it can be proved that variations of 10% in concentration can be regarded as significant from a health point of view.

In order to establish that the red colour was due to 2,4,6-trinitrotoluene rather than to impurities such as isomers of trinitrotoluene, dinitrotoluene, etc., in the standard material, a standard solution containing 0.500 gm. of crude T.N.T. in 250 cc. of acetone was made up, and various dilutions of this standard solution were treated with the hydroxide solution. Similar dilutions of pure 2,4,6-trinitrotoluene in acetone were prepared. No difference in colour was perceptible between comparable solutions prepared from the crude and pure materials. Hence, it would appear unlikely that the colour could be due to substances other than 2,4,6-trinitrotoluene. As further confirmation, it was found that in workroom tests in which air containing 2,4,6-trinitrotoluene was passed through acetone the same colour reaction and shade were obtained on treating the absorbing solution with base. In these experiments the likelihood that T.N.T. dust or vaporized impurities were present was remote, since the material was in the molten state and the impurities in the crude T.N.T. would not evaporate at the temperature of 82° C. which was maintained in the T.N.T. pots from which the vapour emanated.

Field Tests

In extending this method of testing to actual air analysis the procedure used was as follows:—

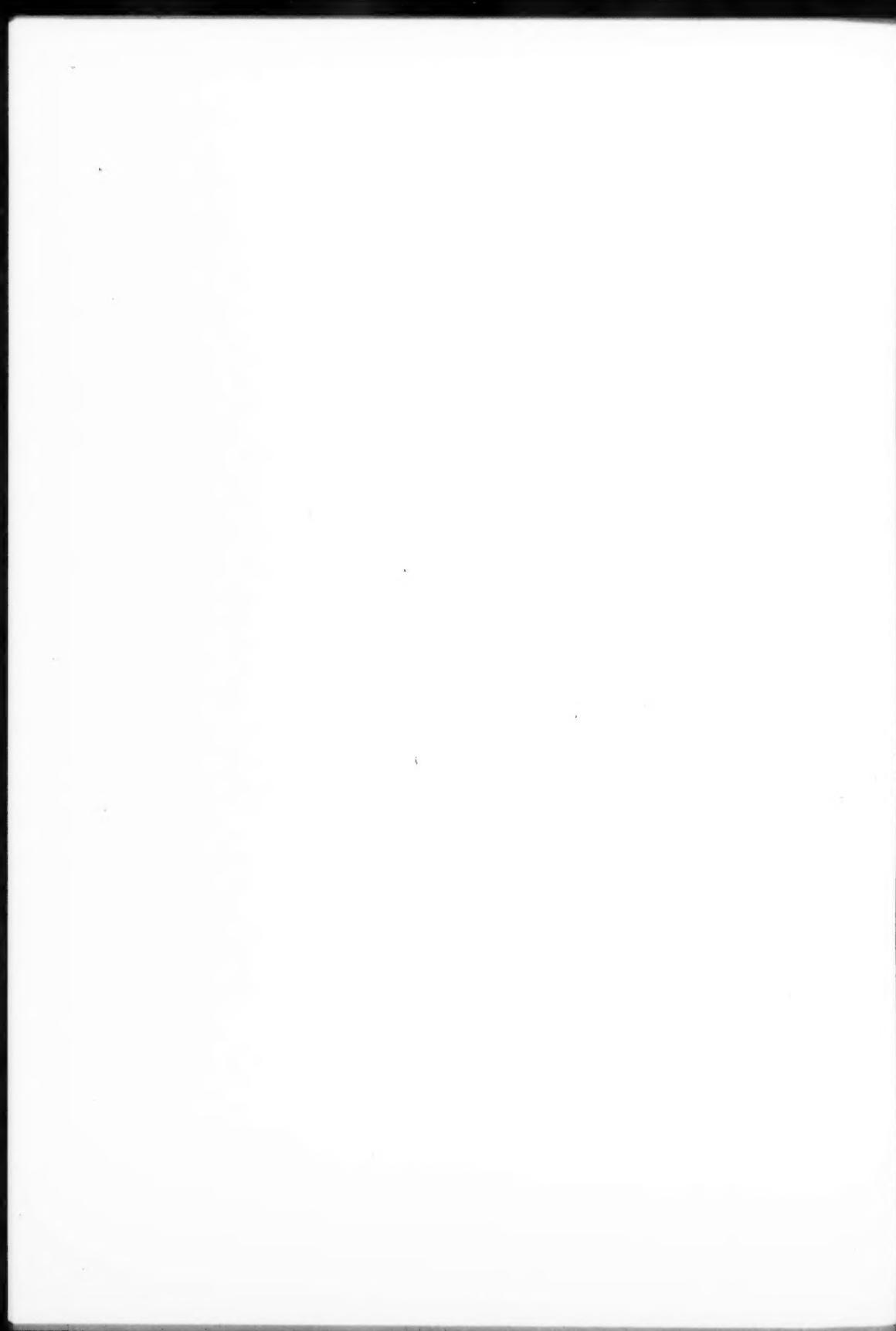
The air was drawn through a sintered glass bubbling tube containing approximately 150 cc. of acetone, at a rate of 0.5 litre per min. (measured by means of a standardized flowmeter), for a period of about one hour. Concomitantly, absorption was carried out using two bubbling tubes set up in series, drawing air from the same point in the room. This procedure eventually showed that one bubbling tube collected all the T.N.T. in a given volume of air.

The acetone solution containing the T.N.T. absorbed from the air was evaporated at a temperature well below 82° C. (to avoid the possibility of the loss of T.N.T., which melts and evaporates above 82° C.). As concentration continued, 1 cc. of the solution being concentrated was withdrawn and tested for the presence of T.N.T. in the manner previously described. This procedure was carried out in order that the concentration of the solution should not be increased by evaporation to such an extent that the reaction obtained with the base would result in a colour outside the range of colour of the standard solutions prepared for comparison.

The method has been employed in numerous plant tests and can be conducted with facility. However, experiments continue to be carried out with a view to cutting the absorption time from one hour to a shorter period. This absorption time, it may be mentioned, is, of course, a function of the concentration of T.N.T. in the air being tested, as enough T.N.T. must be absorbed to provide a concentration greater than 0.000004 gm. of T.N.T. in 1 cc. of concentrated solution. With a few preliminary tests a suitable absorption time can be set.

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